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HIGH ENERGY HALOGEN CHEMISTRY

Kurt Baum, et al

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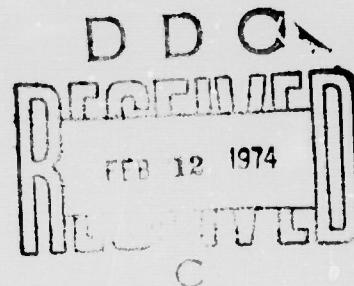
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HIGH ENERGY HALOGEN CHEMISTRY

by

K. Baum, C.D. Beard and V. Grakauskas

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13. ABSTRACT <p>The reaction of primary alkyl iodides with silver perchlorate gave mainly rearranged perchlorates in hydrocarbon or halocarbon solvents but unrearranged products in benzene. Silver triflate gave similar results. Alkyl iodides and dichlorine heptoxide gave alkyl perchlorates and an unidentified material that converted additional alkyl iodide to ether. Alkyl hypochlorites and iodine gave hypoiodites. Halogens and interhalogens reacted with olefins in the presence of dichlorine heptoxide or silver perchlorate to give β-halo perchlorates. Reactions of alcohols, amines and ethers with dichlorine heptoxide are described.</p>			

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I. Introduction

The objective of this research program is to explore the synthesis of new functional groupings with potential utility in high energy propellants and explosives. The major emphasis of this research has been on the preparation of organic derivatives of oxidized halogen compounds.

Appendices to this report describe completed areas of investigation in the format of journal manuscripts. Appendix A deals with the preparation and characterization of alkyl perchlorates from reactions of alcohols with dichlorine heptoxide. Appendix B describes perchlorylamines obtained from amines and dichlorine heptoxide. Appendix C describes reactions of ethers with dichlorine heptoxide and with alkyl perchlorates. Uncompleted work that comprises the body of this report includes reactions of silver perchlorate and of dichlorine heptoxide with alkyl iodides and reactions of silver perchlorate and dichlorine heptoxide with halogens and interhalogens in the presence of olefins.

II. Discussion

A. Reactions of Silver Perchlorate and Silver Triflate with Alkyl Iodides

In connection with the structure proof of alkyl perchlorates obtained from dichlorine heptoxide and alcohols (Appendix A), an independent synthesis was desirable. The only primary alkyl perchlorates with more than two carbon atoms described in the literature were prepared by the reaction of silver perchlorate with alkyl iodides in a hydrocarbon solvent.¹ Isomerization would not have been detected without the availability of nmr. However, reactions of other silver salts, such as the nitrate,^{2,3} toluenesulfonate,⁴ and nitrite,⁵ with alkyl halides have been studied extensively and under similar conditions, only primary substitution products have been reported from primary halides.

It was unexpected, therefore, to find that the reaction of propyl iodide with a suspension of silver perchlorate in carbon tetrachloride, pentane or 1,1,2-trichlorotrifluoroethane gave isopropyl perchlorate as the major product. A quantitative yield of perchlorates was obtained consisting of 60% isopropyl perchlorate and 40% propyl perchlorate. Variables such as the particle size of the silver perchlorate and the rate of stirring resulted in variations as much as 10% in the product distribution but the total yield remained essentially quantitative.

The use of benzene as the solvent resulted in a slower reaction rate; 18 hrs was required for completion but the product, obtained in 91% yield, consisted entirely of propyl perchlorate. No isopropyl perchlorate or benzene alkylation products were detected by nmr or by glpc after reaction with lithium bromide. The use of mixtures of carbon tetrachloride and benzene gave intermediate results. Thus, a solvent consisting of 33% benzene and 67% carbon tetrachloride gave an equal mixture of propyl perchlorate and isopropyl

perchlorate. A solvent consisting of 67% benzene and 33% carbon tetrachloride gave a product containing 15% isopropyl perchlorate and 85% propyl perchlorate.

Since silver perchlorate is soluble in benzene but much less so in the mixed solvents, the possibility was considered that a homogeneous selective reaction competes with a heterogeneous unselective reaction. However, a large excess of silver perchlorate in benzene, mainly out of solution, also gave completely unrearranged perchlorate.

Methylene chloride as solvent gave a product with 62% propyl perchlorate and 38% isopropyl perchlorate. This solvent thus gives results intermediate between those with benzene and with hydrocarbons or carbon tetrachloride.

The use of an excess of propyl iodide, with carbon tetrachloride as the reaction solvent, was also found to reduce the amount of rearrangement. Twice the theoretical amount of propyl iodide gave 41% rearranged product, and four times the theoretical amount of propyl iodide gave only 23% rearrangement.

The difference in selectivity between these silver perchlorate reactions and those of other silver salts would appear to be related to the fact that the perchlorate ion is a poorer nucleophile. Consequently, since the triflate ion is similar in reactivity to the perchlorate ion, the corresponding silver triflate reactions were examined.

The results were quite similar to those of the silver perchlorate reactions. In carbon tetrachloride, pentane or 1,1,2-trichlorotrifluoroethane, the product consisted of 34% propyl triflate and 66% isopropyl triflate. Methylene chloride gave 59% propyl triflate and 41% isopropyl triflate. Benzene gave completely unrearranged propyl triflate. Also, as in the perchlorate reactions, diluted benzene gave intermediate results. Thus, 33% benzene in

1,1,2-trichlorotrifluoroethane gave 57% rearrangement, 50% benzene gave 49% rearrangement, and 67% benzene gave 23% rearrangement. Using ethyl ether as solvent resulted in exchange of alkyl groups. A mixture of products containing ethyl triflate and ethyl propyl ether was obtained. An excess of propyl iodide as solvent gave only unrearranged propyl perchlorate.

The generally accepted mechanism for silver salt displacements is a push-pull mechanism, in which the transition state requires both "pull" on the halogen by silver and "push" by the displacing anion. The degree of pull by silver depends on the nucleophilic power of the anion. For a strong nucleophile, the amount of carbon-halogen bond breaking in the transition state is close to that in an S_N displacement, whereas for a weak nucleophile, the halogen bond must be almost completely ruptured before the new bond begins to form.

Perchlorate and triflate are the least nucleophilic anions that have been studied in silver salt alkylations, so the transition state should be closer to that of an S_N 1 reaction. A 1,2 hydride shift can therefore compete with direct displacement.

The prevention of this rearrangement by the use of benzene, alkyl iodide, or to a lesser extent, methylene chloride as the solvent is more difficult to rationalize. The solvents that lead or do not lead to rearrangement do not fall into a pattern with regard to polarity or dielectric constant. One possible explanation of the results is the reaction of an incipient carbonium ion with solvent to form a complex which then undergoes displacement by the anion. The lack of any byproducts resulting from the alkylation of benzene argues against this mechanism. Furthermore, the formation of a lower-energy

intermediate should accelerate the reaction, whereas the rate is considerably slower in benzene.

The experimental results are more readily explained as a consequence of the well-known complexation of silver ions by benzene. The coordinated silver ions are less reactive and so exert less "pull" on the halogens of the reactant. The complexed halogen is then displaced with a transition state that is more S_N2 -like. Both the reduced reaction rate and the increased regio-specificity are explained on this basis. Results with neat alkyl iodides as solvents can be rationalized similarly on the basis of silver complexation with solvents. Since complexation is an equilibrium phenomenon, intermediate results in mixed solvents are to be expected. This equilibrium also explains the fact that a large excess of silver salt out of solution does not change the results. Surface sites are subject to the same equilibrium deactivation.

Another possible effect of benzene solvation is increased nucleophilic activity of the anion, providing a more S_N2 -like transition state. Furthermore, the heterogeneous reaction requires specific orientation of the substrate with respect to anion sites on the surface. Repeated adsorption-desorption at the silver sites would therefore provide increased possibilities for hydride shift.

Knowledge of the effect of solvent on selectivity allows one to use these reactions for preparative purposes. For substrates that do not undergo facile carbonium ion rearrangement, carbon tetrachloride is a preferred solvent because of the high reaction rates obtainable and for convenience in nmr observation of the reaction course. For substrates prone to rearrangements, benzene provides selectivity. Preparations of perchlorates and of triflates from silver

perchlorate and silver triflate are shown in Tables 1 and 2, respectively. Yields were determined by nmr integration with the addition of a measured amount of a suitable reference material. Yields of the triflates were confirmed by the same procedure using fluorine nmr. Spectral properties of the products were identical with those of the perchlorates (Appendix A) and triflates⁶ obtained from the corresponding alcohols and dichlorine heptoxide or triflic anhydride respectively. Hexyl iodide and silver perchlorate in carbon tetrachloride gave mainly secondary perchlorates, and both 2-hexyl perchlorate and 3-hexyl perchlorate were identified as the corresponding bromides following reaction with lithium bromide.

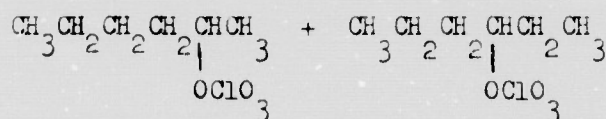
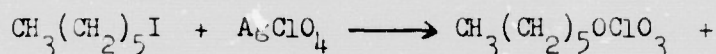


Table 1. Reactions of Alkyl Iodides with Silver Perchlorate

<u>Starting Material</u>	<u>Product</u>	<u>Solvent</u>	<u>Yield (%)</u>
CH_3I	CH_3OCIO_3	CCl_4	81
$\text{CH}_3\text{CH}_2\text{I}$	$\text{CH}_3\text{CH}_2\text{OCIO}_3$	CCl_4	99
$(\text{CH}_3)_2\text{CHI}$	$(\text{CH}_3)_2\text{CHOCIO}_3$	CCl_4	98
$\text{CH}_2=\text{CHCH}_2\text{I}$	$\text{CH}_2=\text{CHCH}_2\text{OCIO}_3$	CCl_4	96
$\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{OCIO}_3$	C_6H_6	91
$\text{CH}_3(\text{CH}_2)_3\text{CH}_2\text{I}$	$\text{CH}_3(\text{CH}_2)_3\text{CH}_2\text{OCIO}_3$	C_6H_6	86
$\text{CH}_3(\text{CH}_2)_8\text{CH}_2\text{I}$	$\text{CH}_3(\text{CH}_2)_8\text{CH}_2\text{OCIO}_3$	C_6H_6	89

Table 2. Reactions of Alkyl Iodides with Silver Triflate

<u>Starting Material</u>	<u>Product</u>	<u>Solvent</u>	<u>Yield (%)</u>
CH_3I	$\text{CH}_3\text{OSO}_2\text{CF}_3$	CCl_4	85
$\text{CH}_3\text{CH}_2\text{I}$	$\text{CH}_3\text{CH}_2\text{OSO}_2\text{CF}_3$	CCl_4	98
$(\text{CH}_3)_2\text{CHI}$	$(\text{CH}_3)_2\text{CHOSO}_2\text{CF}_3$	CCl_4	97
$\text{CH}_2=\text{CHCH}_2\text{I}$	$\text{CH}_2=\text{CHCH}_2\text{OSO}_2\text{CF}_3$	CCl_4	95
$\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{OSO}_2\text{CF}_3$	C_6H_6	92
$\text{CH}_3(\text{CH}_2)_3\text{CH}_2\text{I}$	$\text{CH}_3(\text{CH}_2)_3\text{CH}_2\text{OSO}_2\text{CF}_3$	C_6H_6	82
$\text{CH}_3(\text{CH}_2)_8\text{CH}_2\text{I}$	$\text{CH}_3(\text{CH}_2)_8\text{CH}_2\text{OSO}_2\text{CF}_3$	C_6H_6	93

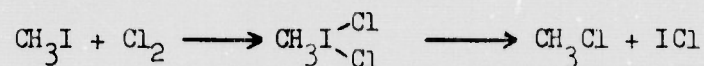
B. Reactions of Alkyl Iodides with Dichlorine Heptoxide.

In a continuation of the screening of dichlorine heptoxide reactions with organic compounds containing various functional groups⁷, alkyl iodides were examined.

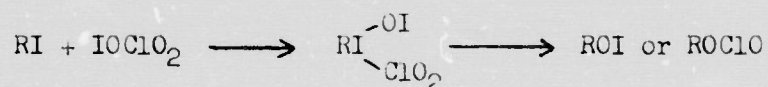
Ethyl iodide reacted rapidly with a solution of dichlorine heptoxide in carbon tetrachloride at 0°. Equimolar amounts of the reagents gave a 63% yield of ethyl perchlorate, a 10% yield of ethyl acetate and a 3% yield of diethyl ether. To gain insight into the course of this reaction various ratios of the reactants were examined. A 2:1 molar ratio of ethyl iodide to dichlorine heptoxide gave a 66% yield of ethyl perchlorate and 11% yield of ethyl acetate and a 21% yield of diethyl ether. These yields are expressed in moles of product per mole of dichlorine heptoxide. Thus, the main product arising from the addition of a second mole of ethyl iodide is diethyl ether. A third mole of ethyl iodide resulted in no further change. An excess of dichlorine heptoxide resulted in no diethyl ether being formed.

These results suggest that the initial reaction gives alkyl perchlorate and a reactive intermediate not visible by nmr. This intermediate and additional alkyl iodide give ether.

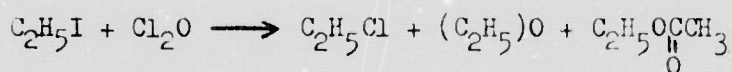
One might expect the reaction to take place by way of valence expansion of the iodine since chlorination takes place by this route. Methyl iodide was reported⁸ to form the dichloride at low temperatures, which decomposes at -30° to form methyl chloride and ICl.



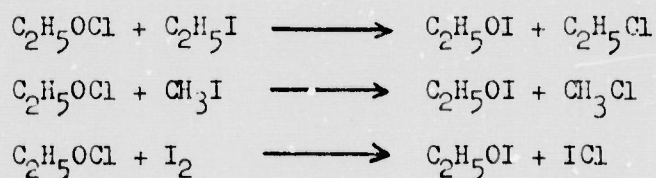
A similar route may be envisioned for the formation of an alkyl perchlorate from an iodide and Cl_2O_7 . The other fragment would be IClO_3 or IOClO_2 . Addition of this fragment to alkyl iodide and decomposition of the adduct would give a reactive alkoxy derivative such as the hypiodite or chlorite:



Information as to the types of alkoxy derivatives that could possibly be involved was obtained by using model compounds. Chlorine oxide in carbon tetrachloride was thus treated with ethyl iodide. The products were ethyl chloride (40% yield), diethyl ether (10%) and ethyl acetate (4%).



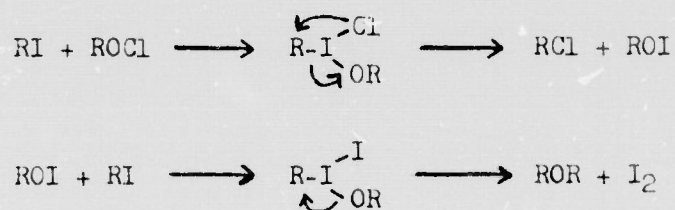
Ethyl hypochlorite in carbon tetrachloride solution was prepared by the literature method⁹. Reaction of this compound with two moles of ethyl iodide gave ethyl chloride (82% yield), ethyl acetate (4%) and diethyl ether (37%). The use of equimolar amounts of the reagents gave a quantitative yield of ethyl chloride and a new compound, which, on the basis of its nmr and ir spectra, was assigned the structure, ethyl hypiodite. The same compound was obtained from ethyl hypochlorite and methyl iodide. In this case the other product, methyl chloride, was readily removed under vacuum to give a solution containing only ethyl hypiodite. The same compound was also obtained from ethyl hypochlorite and iodine.



Ethyl hypoiodite in carbon tetrachloride was decomposed in several hours, liberating iodine. In the presence of water it decomposed rapidly. The compound reacted with an equimolar amount of ethyl iodide to give diethyl ether in 41% yield and ethyl acetate in 12% yield.

The product mixture from ethyl hypoiodite and ethyl iodide is thus similar to that arising from the addition of a second mole of ethyl iodide to the ethyl iodide - Cl_2O_7 reaction mixture. Ethyl hypoiodite or another R-O-X type intermediate is implicated, but R-O-Cl cannot be the intermediate since hypochlorites gave mainly alkyl chlorides when reacted with iodides. The results are not definitive but are consistent with ClO_3I as the initial product.

The formation of hypoiodite from hypochlorite, and the formation of ether from iodide and hypoiodite can be rationalized on the basis of trivalent iodine intermediates as follows:



Similar results were obtained with other alkyl iodides and dichlorine heptoxide. Thus methyl iodide gave methyl perchlorate in 73% yield and dimethyl ether in 12% yield with 1 mol of Cl_2O_7 . With a 2:1 ratio of iodide to Cl_2O_7 , the yield of ether was increased to 35%. Propyl iodide with 1 mol of Cl_2O_7 gave propyl perchlorate (61%), isopropyl perchlorate (9%), propyl propionate (9%) and dipropyl ether (2%). A higher ratio of iodide to Cl_2O_7 increased the ether yield. Isopropyl iodide with an equimolar amount of Cl_2O_7 gave only isopropyl perchlorate (74% yield), but with excess iodide, isopropyl ether,

isopropanol, and 2,2-diperchloratopropane were also formed. Pentyl iodide and hexyl iodide gave the corresponding perchlorates with 1 mol of Cl_2O_7 . In all of these reactions an insoluble white solid was also formed that was not identified.

Iodobenzene also reacted with Cl_2O_7 at 0° to give a white solid that became blue-green and then white again. The final material was stable, but the composition is not yet known. When the reaction was carried out at room temperature, the initial precipitate exploded. Perfluoroheptyl iodide reacted with Cl_2O_7 in CCl_4 under reflux or after prolonged standing at room temperature to give a white solid. Trifluoroethyl iodide reacted slowly with Cl_2O_7 to give an unidentified insoluble oil. The carbon tetrachloride solution contained a compound tentatively identified (ir and nmr) as trifluoroethyl chloroformate, suggestive of attack on the solvent.

An attempt was made to trap intermediates in the reaction of fluorinated iodides with Cl_2O_7 by the addition of an olefin. Addition of ethylene to a solution of trifluoroethyl iodide and Cl_2O_7 in carbon tetrachloride gave ethylene diperchlorate, 2-chloroethyl perchlorate and ethyl perchlorate. Only a trace of the iodide was required to promote this reaction, whereas no reaction took place between Cl_2O_7 and ethylene in the absence of the iodide under the same conditions. More reactive olefins gave similar products directly⁷. Thus, trifluoroethyl iodide appears to function as a catalyst to promote the reactivity of Cl_2O_7 . Perfluoroheptyl iodide and pentafluoroiodobenzene had similar catalytic effects.

Another olefin that did not react directly with Cl_2O_7 in CCl_4 was 1,1-difluoroethylene. In the presence of trifluoroethyl iodide, however, 2-chloro-

1,1-difluoroethyl perchlorate, and 1,1-difluoroethyl perchlorate, as well as a trace of 2-iodo-1,1-difluoroethyl perchlorate were formed.

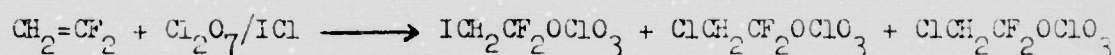
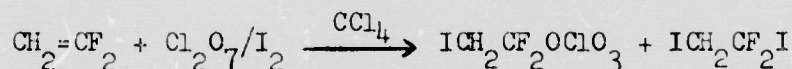
C. Reactions of Dichlorine Heptoxide-Halogen and Silver Perchlorate-Halogen Mixtures with Olefins

Reactions of alkyl iodides with dichlorine heptoxide above were suggestive of trivalent iodine reactive intermediates. Michael and Conn, in 1901, reported a vigorous reaction between dichlorine heptoxide and iodine to give a white powder that fumed in air¹⁰. A reinvestigation of this reaction was of interest, both from the standpoint of the type of bonding involved and from the standpoint of finding a useful synthetic reagent.

When iodine was added to a carbon tetrachloride solution of dichlorine heptoxide, the iodine was consumed over a 1 hr period to give a white solid and a pale yellow solution. Equal molar amounts of the reagents were consumed. The solid appeared to be iodine pentoxide, but preliminary analytical results were erratic. Iodine chloride also reacted with dichlorine heptoxide to give a solution and a solid with appearance similar to those from iodine. Iodine bromide reacted only very slowly with dichlorine heptoxide, and chlorine and bromine gave no evidence of reaction. To obtain information regarding the soluble products from iodine and from iodine chloride, reactions with olefins were studied. In-situ reactions of halogens and dichlorine heptoxide with olefins were also studied.

1,1-Difluoroethylene reacted with the soluble product from iodine and dichlorine heptoxide to give 2-iodo-1,1-difluoroethyl perchlorate in 40-60% yields, as well as small amounts of 1,1-difluoro-1,2-diiodoethane. The iodine chloride product reacted similarly to give in 65-75% yield a mixture of 2-chloro-1,1-difluoroethyl perchlorate and 2-iodo-1,1-difluoroethyl perchlorate. The latter was the major product. The compounds were identified

by nmr and ir spectra, as well as by quantitative analysis for hydrogen and fluorine by nmr.

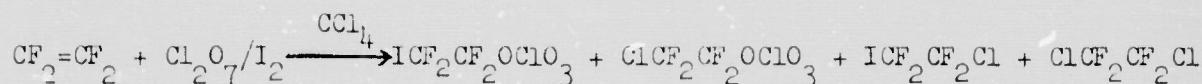


Ethylene also reacted with either iodine-dichlorine heptoxide or iodine chloride-dichlorine heptoxide to give 2-iodoethyl perchlorate in 10-15% yields. The major products were 1,2-diiodoethane and 1-chloro-2-iodoethane, respectively. Ethylene also reacted rapidly with dichlorine heptoxide when chlorine or bromine was added, to give the corresponding 2-haloethyl perchlorates in 10-15% yield. Again, the 1,2-dihaloethanes were the major products. These perchlorates were identified by comparison with authentic samples prepared from the corresponding alcohols and dichlorine heptoxide.

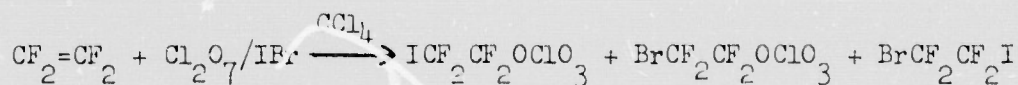
2-Chloro-1,1-difluoroethyl perchlorate was obtained in 50% yield from the reaction of equimolar amounts of 1,1-difluoroethylene, dichlorine heptoxide and chlorine. Smaller amounts of 1,2-dichloro-1,1-difluoroethane and 1,1-difluoroethyl perchlorate were also obtained.

Tetrafluoroethylene also reacted readily with dichlorine heptoxide-halogen mixtures. The major reaction products with dichlorine heptoxide-iodine were identified as 2-chlorotetrafluoroethyl perchlorate and 2-iodotetrafluoroethyl perchlorate. These two compounds were identified by comparing their fluorine nmr spectra with those reported for 2-chlorotetrafluoroethyl perchlorate¹¹ and 2-iodotetrafluoroethyl perchlorate¹². Smaller amounts of 1-chloro-2-iodotetrafluoroethane and 1,2-dichlorotetrafluoro-

ethane were also produced in this reaction:



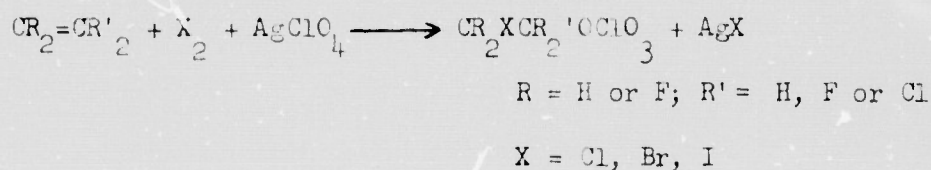
Dichlorine heptoxide-iodine chloride also reacted with tetrafluoroethylene to give a 50-60% yield of 2-chlorotetrafluoroethyl perchlorate and much smaller amounts of 1,2-dichloro- and 1-chloro-2-iodotetrafluoroethanes. No 2-iodotetrafluoroethyl perchlorate was obtained in this reaction. On the other hand, the reaction of tetrafluoroethylene with dichlorine heptoxide-iodine bromide yielded both 2-bromotetrafluoroethyl perchlorate and 2-iodotetrafluoroethyl perchlorate, each in 30-40% yield. The identification of 2-bromotetrafluoroethyl perchlorate is tentative and is based on the similarity of its fluorine nmr spectrum (two triplets at δ 67.9 and 91.8) with those of 2-chloro- and 2-bromotetrafluoroethyl perchlorates. A small amount of 1-bromo-2-iodotetrafluoroethane was also produced in this reaction.



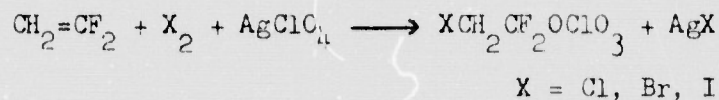
Additional work is in progress to determine the course of these reactions. The reaction of dichlorine heptoxide with iodine is of particular interest since it gives an intermediate that is relatively stable in solution and gives olefin adducts of the elements of iodine perchlorate. Iodine perchlorate is the only unknown member of the family of halogen perchlorates. Reactions of chlorine and of bromine with olefins and dichlorine heptoxide would appear to take place by perchlorate trapping of halonium ions or halogen-olefin complexes, since there is no evidence of a reaction between the halogens and dichlorine heptoxide. These reactions are of interest as a practical route to β -halo perchlorates, previously obtainable only from halogen perchlorates.

A related route to this type of product is the reaction of silver perchlorate with halogens. The reaction between silver perchlorate and iodine has been studied by a number of workers¹³. In inert solvents such as carbon tetrachloride, no reaction occurs¹⁴ whereas more reactive solvents are attacked. Recently, Christie and Schack failed to synthesize iodine perchlorate by reacting iodine with chlorine perchlorate, but obtained iodine tris(perchlorate)¹⁵.

Although no visible reaction occurs between anhydrous silver perchlorate and iodine, perchlorates are readily produced when an olefin is added to the mixture. Ethylene, 1,1-difluoroethylene, tetrafluoroethylene, and 1,1-dichloroethylene were the olefins employed in the study of these reactions which proceeded by the following general equation:

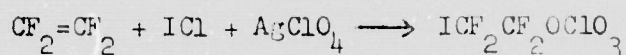


In most cases, these reactions yield the same products as dichlorine heptoxide-halogen mixtures, but silver perchlorate reactions generally yield only one product. Thus, stoichiometric mixtures of chlorine, bromine or iodine and silver perchlorate reacted when 1,1-difluoroethylene to give 2-chloro-1,1-difluoroethyl, 2-bromo-1,1-difluoroethyl, and 2-iodo-1,1-difluoroethyl perchlorates, respectively, in 95-98% yields:

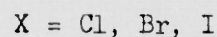
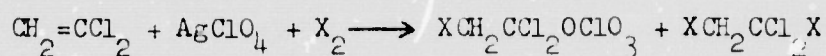


2-Iodo-1,1-difluoroethyl perchlorate was also obtained by using iodine chloride or iodine bromide in the above reaction. These reactions were completed in 15-60 min at room temperature. Carbon tetrachloride or methylene chloride are convenient solvents for these reactions and silver perchlorate must be scrupulously dehydrated before use.

Silver perchlorate-halogen mixtures are somewhat less reactive with olefins than dichlorine heptoxide-halogen mixtures. Thus, whereas the reaction with dichlorine heptoxide and tetrafluoroethylene took place with iodine, iodine chloride or iodine bromide, only iodine chloride was reactive with silver perchlorate.



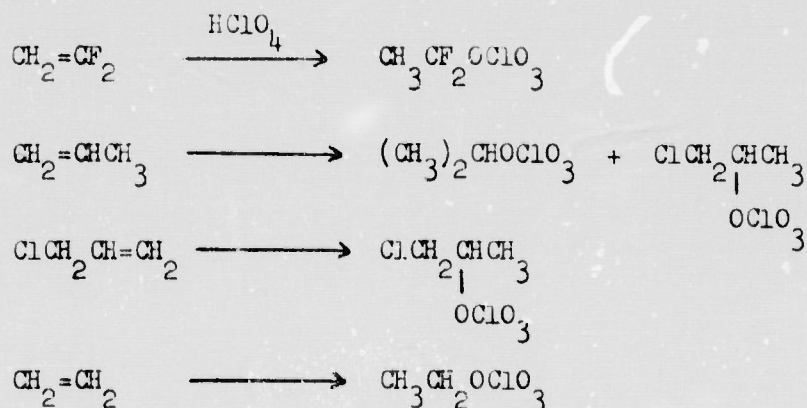
2-Iodoethyl perchlorate was obtained in good yields when iodine, iodine chloride, or iodine bromide and silver perchlorate mixtures were reacted with ethylene. 1,1-Dichloroethylene also reacted with silver perchlorate-halogen mixtures to give the corresponding 2-halo-1,1-dichloroethyl perchlorates and 1,2-dihalo-1,1-dichloroethane:



The tetrahaloalkanes were identified by comparing their nmr spectra with those of the authentic compounds. The identification of 2-halo-1,1-dichloroethyl perchlorates is tentative and is based on infrared and proton nmr spectra of the compounds.

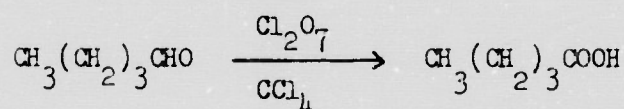
D. Miscellaneous Reactions

Reactions of simple olefins with dichlorine heptoxide in carbon tetrachloride were described previously⁷. Extension of this reaction to 1,1-difluoroethylene resulted only in the formation of a low yield of 1,1-difluoroethyl perchlorate, apparently formed from perchloric acid present as an impurity. Subsequently, water was added to dichlorine heptoxide solution in carbon tetrachloride as a convenient source of small quantities of anhydrous perchloric acid. This reagent and 1,1-difluoroethylene gave a 76% yield of 1,1-difluoroethyl perchlorate. Propene similarly gave a 65% yield of isopropyl perchlorate and a 10% yield of 1-chloro-2-propyl perchlorate, a product previously obtained from propene and dichlorine heptoxide⁷. Allyl chloride and the perchloric acid reagent gave a 91% yield of 1-chloro-2-propyl perchlorate. Ethylene gave a 63% yield of ethyl perchlorate, whereas 1,1-dichloroethylene did not react.

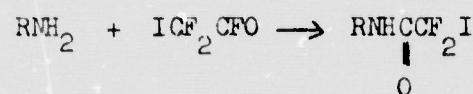
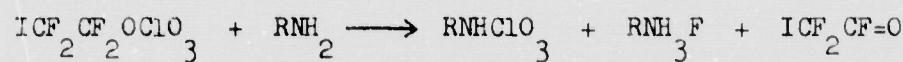
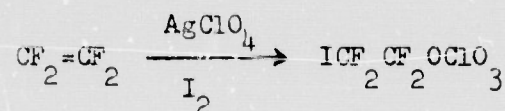


Reactions of ketones with dichlorine heptoxide to give geminal diperchlorates were described previously⁷. Attempts to extend this reaction to aldehydes resulted in the formation of high yields of carboxylic acids. Valeraldehyde gave an 86% yield of valeric acid, and pivaldehyde gave an 81% yield of pivalic

acid. Dichlorine heptoxide also functioned as an oxidizing agent for nitroso compounds. Thus nitrosobenzene gave a 96% yield of nitrobenzene.



Attack of nucleophiles on the chlorine of a perchlorate group was examined as a mild perchlorylation reaction. Perhalogenated perchlorates offer the advantages of reduced tendency for attack on carbon by the nucleophile, and inability to undergo perchloric acid elimination. An easily available perchlorate of this type is 2-iodotetrafluoroethyl perchlorate, prepared by mixing iodine, silver perchlorate and tetrafluoroethylene. The reaction of this compound with hexylamine gave N-perchlorylhexylamine and N-hexyl-1,1-difluoro-1-iodoacetamide:



III. Experimental

A. Reactions of Silver Perchlorate and Silver Triflate with Alkyl Iodides.

Reaction of Silver Perchlorate with Propyl Iodide. Commercial silver perchlorate was dried azeotropically before use¹. Propyl iodide (0.170 g, 1 mmol) was added with stirring to 0.207 g (1 mmol) of silver perchlorate and 3 ml of carbon tetrachloride at 0°. The mixture was stirred for 1 hr and filtered. Nmr analysis of the solution, using chlorobenzene as a quantitative standard showed a quantitative yield of a mixture of propyl perchlorate (40%) and isopropyl perchlorate (60%). Variables in this heterogeneous reaction that are difficult to reproduce, i.e., particle use of the silver perchlorate and the rate of stirring, resulted in variations of $\pm 10\%$ in the yields of the components, but the total was quantitative. Identical results were obtained when using pentane or 1,1,2-trichlorotrifluoroethane as the solvent. Methylene chloride gave a 92% yield of a mixture of propyl perchlorate (62%) and isopropyl perchlorate (38%). In an experiment identical to that above using carbon tetrachloride, but with twice the theoretical amount of propyl iodide, the product consisted of 41% isopropyl perchlorate and 59% propyl perchlorate. Four times the theoretical amount of propyl iodide gave 23% isopropyl perchlorate and 77% propyl perchlorate.

The use of benzene as the reaction solvent required a reaction period of 18 hrs at room temperature, with stirring. The benzene solution was filtered, washed with water, and dried over magnesium sulfate. Nmr analysis showed a 91% yield of propyl perchlorate and no trace of isopropyl perchlorate or cumene. The benzene solution was added to an equal volume of 10% lithium bromide in acetone, washed with water and dried. Nmr and glpc showed propyl

bromide but no isopropyl bromide. No rearrangement was observed when ten times the theoretical amount of silver perchlorate (2.07 g) was used, mainly out of solution¹⁶.

The reaction of equivalent amounts of propyl iodide and silver perchlorate for 18 hrs, as above, in a solvent consisting of 33% benzene and 67% carbon tetrachloride gave a 90% yield of perchlorates consisting of 50% propyl perchlorate and 50% isopropyl perchlorate. A solvent consisting of 67% benzene and 33% carbon tetrachloride gave a 91% yield consisting of 15% isopropyl perchlorate and 85% propyl perchlorate.

Propyl perchlorate and isopropyl perchlorate were unchanged in control experiments in the presence of silver perchlorate and silver iodide.

Reaction of Hexyl Iodide with Silver Perchlorate in Carbon Tetrachloride. The above procedure was used. Nmr analysis showed that the product consisted of 42% 1-hexyl perchlorate and 58% secondary perchlorates. In this mixture the relative amounts of 2-hexyl perchlorate and 3-hexyl perchlorate could not be determined. The mixture was added to an equal volume of lithium bromide in acetone and washed with water. A mixture of 2-bromohexane and 3-bromohexane was isolated by preparative glpc. Nmr analysis, by comparison with authentic samples, showed a 4:1 ratio of 2-bromohexane to 3-bromohexane.

In control experiments, 1-hexyl perchlorate gave a quantitative yield of 1-bromohexane, and the secondary isomers gave a 50% yield of the corresponding bromide.

Reaction of Silver Triflate with Propyl Iodide. Propyl iodide (0.170 g, 1.0 mmol) was added with stirring to 0.257 g (1.0 mmol) of silver triflate in 3 ml of carbon tetrachloride at room temperature. The mixture was stirred for 2 hrs and was filtered. Yields were determined by both proton and fluorine nmr using benzotrifluoride as a quantitative standard. A 97% yield of triflates was obtained consisting of 34% propyl triflate and 66% isopropyl triflate. The yields of the components varied $\pm 10\%$ but the total was always nearly quantitative. The same results were obtained using 1,1,2-trichlorotrifluoroethane or pentane as the reaction solvent. Methylene chloride gave a 95% yield consisting of 59% propyl triflate and 41% isopropyl triflate. Using benzene as solvent, with an 18 hr reaction period gave a 92% yield of propyl triflate with no isopropyl triflate. A solvent consisting of 33% benzene and 67% 1,1,2-trichlorotrifluoroethane gave a 98% yield containing 43% propyl triflate and 57% isopropyl triflate; 50% benzene, 50% 1,1,2-trichlorotrifluoroethane gave a 98% yield with 51% propyl triflate, 49% isopropyl triflate; 67% benzene, 33% 1,1,2-trichlorotrifluoroethane gave a 94% yield with 77% propyl triflate, 23% isopropyl triflate.

Using ethyl ether as solvent gave a mixture of products containing ethyl triflate and ethyl propyl ether.

Propyl Triflate. A solution of 0.30 g (5 mmol) of propanol and 0.395 g (5 mmol) of pyridine in 5 ml of carbon tetrachloride was added dropwise, with stirring to a solution of 1.41 g (5 mmol) of triflic anhydride in 10 ml of carbon tetrachloride at 0°. In 15 min the solution was filtered, washed with water, and dried over magnesium sulfate. Nmr analysis using chlorobenzene as a quantitative reference, showed an 86% yield of propyl triflate: proton nmr

(CCl₄) δ 4.45 (t, 2H, J=6 Hz, CH₂O-), 1.83 (m, 2H, CH₂CH₂O-) and 1.08 ppm (t, 3H, J=6 Hz, CH₃); fluorine nmr (CCl₄) δ 75.80 ppm (s); ir (CCl₄) 2990 (m), 1460 (w), 1420 (vs), 1250 (s), 1220 (vs), 1155 (vs) and 950 cm⁻¹(vs).

Pentyl Triflate. Pentyl iodide (0.91 g, 4.6 mmol) was added dropwise with stirring to a partial solution of 2.40 g (8 mmol) of silver triflate in 25 ml of benzene. The mixture was stirred for 18 hrs and filtered. The filtrate was washed with water, dried over magnesium sulfate and distilled to give 0.785 g (82%) of pentyl triflate, bp 55-57 (1.5 mm), with spectra identical with those in the literature⁶.

Decyl Triflate. Decyl iodide (4.02 g, 15 mmol) was reacted by the above procedure with 5.14 g (20 mmol) of silver triflate in 100 ml of benzene. The washed and dried benzene solution was filtered through silicic acid and stripped of solvent to give 4.05 g (93%) of decyl triflate, a colorless oil: proton nmr (CDCl₃) δ 4.42 (t, 2H, J=6 Hz, CH₂O-), 1.82 (m, 2H, CH₂CH₂O-), 1.27 (m, 14H, CH₂) and 0.83 ppm (m, 3H, CH₃); fluorine nmr δ 75.4 (s); ir (CCl₄) 1420, 1220, 1160 and 950 cm⁻¹ (SO₃CF₃).

Anal. Calcd for C₁₁H₂₁F₃SO₃: C, 45.50; H, 7.29; S, 11.05. Found: C, 45.55; H, 7.09; S, 11.40.

B. Reactions of Alkyl Iodides with Dichlorine Heptoxide.

Reaction of Ethyl Iodide with Dichlorine Heptoxide. Ethyl iodide (0.0936 g, 6 mmol) was added dropwise with stirring at 0° to 2 ml of 0.3 M dichlorine heptoxide in carbon tetrachloride. A granular, colorless precipitate and a purple solution formed immediately. Nmr analysis of the solution showed that the ethyl iodide was consumed in 15 min to give ethyl perchlorate (63% yield), ethyl acetate (10%) and diethyl ether (3%). The products were identified by comparison with authentic samples by nmr, ir, and, for ethyl acetate and ether, glpc retention times.

In a similar experiment using 2 moles of ethyl iodide per mole of Cl_2O_7 , the ethyl iodide was consumed completely to give ethyl perchlorate (66% yield, mols product per mol of Cl_2O_7), ethyl acetate (11%) and diethyl ether (21%). Using 3 moles of ethyl iodide per mole of Cl_2O_7 gave the same yields and 1 mole of ethyl iodide was left unchanged.

Variations of reaction temperature (-20° to +25°) did not appreciably affect product ratios. A twofold excess of dichlorine heptoxide gave a 77% yield of ethyl perchlorate, a 9% yield of ethyl acetate and no ethyl ether.

Reaction of Ethyl Iodide with Chlorine Oxide. Ethyl iodide (0.0936 g, 6 mmol) was added with stirring at 0° to 1 ml of 0.3 M chlorine oxide¹⁷ in carbon tetrachloride to give a purple solution containing (nmr analysis, mols per mol Cl_2O) ethyl chloride (40%), diethyl ether (10%) and ethyl acetate (4%).

Reaction of Ethyl Iodide and Methyl Iodide with Ethyl Hypochlorite.
A 0.3 M solution of ethyl hypochlorite in carbon tetrachloride was prepared

by the reported procedure⁹: nmr (CCl_4) δ 3.37 (q, 2 H, $J = 6.5$ Hz, CH_2) and 1.30 ppm (t, 3 H, $J = 6.5$ Hz, CH_3); ir (CCl_4) 3010 (m), 2960 (m), 1385 (m), 1120 (m), 1030 (s) and 990 cm^{-1} (w).

Ethyl iodide (0.0936 g, 0.6 mmol) was added to 1 ml of this solution with stirring at 0° . Ethyl iodide was consumed in 1 hr to give a purple solution containing ethyl chloride (82%, mols per mol ethyl hypochlorite, nmr analysis) ethyl acetate (11%) and diethyl ether (37%).

A similar experiment using 0.3 mmol of ethyl iodide gave a quantitative yield of ethyl chloride and a compound having a methylene quartet at δ 4.37, tentatively identified as ethyl hypoiodite.

The latter compound was also obtained when methyl iodide was substituted for ethyl iodide in the above experiment. The resulting methyl chloride was removed in vacuo to give a colorless solution of ethyl hypoiodite: nmr (CCl_4) δ 4.37 (q, 2 H, $J = 6.5$ Hz, CH_2) and 1.32 ppm (t, 3 H, $J = 6.5$ Hz, CH_3); ir (CCl_4) 2970 (m), 1480 (m), 1450 (w), 1270 (m), 1240 (m), 1010 (s) and 870 cm^{-1} . The compound decomposed in several hours at room temperature liberating iodine. It was decomposed on washing with water. The same compound, contaminated by ICl, was obtained by adding an equivalent of iodine to ethyl hypochlorite in carbon tetrachloride.

A solution containing 0.3 mmol of ethyl hypoiodite was prepared as above from methyl iodide, and 0.3 mmol of ethyl iodide was added to give ethyl acetate (12%) and diethyl ether (41%). In a control experiment, diethyl ether did not react with ethyl hypochlorite in 72 hrs.

Reaction of Methyl Iodide with Dichlorine Heptoxide. Methyl iodide (0.085 g, 0.6 mmol) was added to 2 ml of 0.3 M dichlorine heptoxide in carbon

tetrachloride with stirring at 0°. After 15 min the solution was filtered. Nmr analysis showed methyl perchlorate (73%) and dimethyl ether (12%). Under the same conditions, using twice this amount of methyl iodide gave methyl perchlorate (70%) and dimethyl ether (35%).

Reaction of Propyl Iodide with Dichlorine Heptoxide. Propyl iodide (0.102 g, 0.6 mmol) was added dropwise with stirring to 2 ml of 0.3 M dichlorine heptoxide in carbon tetrachloride at 0°. An immediate reaction gave a white precipitate and a purple solution. Nmr analysis of the solution showed propyl perchlorate (61% yield, mols product per mol Cl_2O_7), isopropyl perchlorate (9%) propyl propionate (9%) and dipropyl ether (2%). In a similar experiment using twice the above amount of propyl iodide, the yields were unchanged except that of propyl ether (29%).

Reaction of Isopropyl Iodide with Dichlorine Heptoxide. Isopropyl iodide (0.102 g, 0.6 mmol) and dichlorine heptoxide (0.6 mmol) were reacted as above to give isopropyl perchlorate (74%) with only trace impurities detectable by nmr. Twice this amount of isopropyl iodide gave isopropyl perchlorate (71%), isopropyl ether (16%), isopropanol (28%) and 2,2-diperchloratopropane¹⁸ (3%).

Reaction of Pentyl Iodide with Dichlorine Heptoxide. Pentyl iodide (0.1188 g, 0.6 mmol) and dichlorine heptoxide (0.6 mmol) by this procedure gave pentyl perchlorate (76%) with traces of ester and ether impurities. In this case, the white precipitate was washed with carbon tetrachloride and dried under vacuum: mp > 300° (the mp of iodine pentoxide is 300-325° dec).

Anal. Calcd for I_2O_5 : I 76.03. Found: I 70.87; Cl < 0.1%.

Reaction of Hexyl Iodide with Dichlorine Heptoxide. Hexyl iodide (0.1272 g, 0.6 mmol) was added to 2 ml of 0.3 M dichlorine heptoxide in carbon tetrachloride with stirring at 0°. Nmr analysis of the filtered solution showed a 54% yield of hexyl perchlorate. The solution was added dropwise to an equal volume of 10% lithium bromide in acetone. Acetone was removed by repeated washing with water. Nmr analysis of the solution showed a 49% overall yield of hexyl bromide (91% based on hexyl perchlorate).

Another experiment using twice the above amount of hexyl iodide gave hexyl perchlorate (56%, mols per mol of dichlorine heptoxide) dihexyl ether (37%) and an unidentified carbonyl-containing compound (ca. 5%). The solution was treated with lithium bromide and with water as above. Hexyl bromide and dihexyl ether were isolated by glpc (6 ft x 1/4 in column of 12% QF-1 on chromosorb W, 75°) and identified by retention time and spectra.

Reaction of Iodobenzene with Dichlorine Heptoxide. Iodobenzene (0.122 g, 0.6 mmol) was added at 0° with stirring to 2 ml of 0.3 M dichlorine heptoxide in carbon tetrachloride. A white solid separated which became blue-green in 15-20 min and white again after 10 min. This solid was insensitive to shock and was stable for several weeks at room temperature. The carbon tetrachloride solution showed no nmr signals. The solid was washed with carbon tetrachloride and dried under vacuum: mp 45-55° d. This solid was insoluble in most common solvents, but reacted rapidly with dimethyl sulfoxide and slowly with methanol. The ir spectrum showed strong bands at 3400 and 1100 cm⁻¹.

Anal. Found: C, 16.63; H, 1.84; Cl, 11.75; I, 40.84.

When the addition of iodobenzene to the dichlorine heptoxide solution was carried out at room temperature, the initial precipitate exploded.

Reaction of Perfluoroheptyl Iodide with Dichlorine Heptoxide.

Perfluoroheptyl iodide (0.298 g, 0.6 mmol) was heated under reflux for 3 hrs with 2 ml of 0.3 M dichlorine heptoxide in carbon tetrachloride. A white solid was formed in about 20% conversion. The solution contained starting material and about 5% of a carbonyl-containing material (1715 cm^{-1}). The same products were formed when the reactants were stirred for 6 wks at ambient temperature. The structures are under investigation.

Reaction of Trifluoroethyl Iodide with Dichlorine Heptoxide.

Trifluoroethyl iodide (0.186 g, 0.6 mmol) was stirred with 2 ml of 0.3 M dichlorine heptoxide in carbon tetrachloride for 18 hrs at room temperature. The starting material was consumed and an orange-red oil separated. The carbon tetrachloride layer was removed and fresh carbon tetrachloride and water were added. Nmr and ir spectra showed a 35% regeneration of trifluoroethyl iodide. The original carbon tetrachloride solution contained a 16% yield of a compound tentatively identified as trifluoroethyl chloroformate: proton nmr (CCl_4) δ 4.80 (q, $J_{\text{HF}} = 7\text{ Hz}$, CF_3CH_2); fluorine nmr (CCl_4) δ 78.08 ppm (t, $J_{\text{HF}} + 7\text{ Hz}$, CF_3CH_2); ir (CCl_4) 1710 (s), 1125 (vs).

Reaction of Trifluoroethyl Iodide and Ethylene with Dichlorine Heptoxide. Ethylene (14 ml, 0.6 mmol) was added by syringe to a partially

evacuated flask containing 0.186 g (0.6 mmol) of trifluoroethyl iodide and 2 ml of 0.3 M dichlorine heptoxide in carbon tetrachloride, and the mixture was stirred for 18 hrs at room temperature. No insoluble material was formed. The mixture was stirred with water and the carbon tetrachloride layer was dried over magnesium sulfate. Nmr analysis using chlorobenzene as a quantitative standard showed ethylene diperchlorate (16%), 2-chloroethyl perchlorate (33%), trifluoroethyl iodide (78%) and ethyl perchlorate (4%). The perchlorates were identified by ir, nmr and glpc comparison with authentic samples prepared from the corresponding alcohols.

An otherwise identical experiment with only 0.06 mmol of trifluoroethyl iodide gave ethylene diperchlorate (20%), 2-chloroethyl perchlorate (33%), trifluoroethyl iodide (7%) and ethyl perchlorate (8%).

Ethylene did not react with dichlorine heptoxide under these conditions in the absence of an iodide.

Reaction of Perfluoroheptyl Iodide and Ethylene with Dichlorine Heptoxide. Under the above conditions, equimolar quantities of ethylene, dichlorine heptoxide and perfluoroheptyl iodide gave ethylene diperchlorate (7%), 2-chloroethyl perchlorate (11%), perfluoroheptyl iodide (90%) and ethyl perchlorate (14%). The ethylene was not completely consumed.

Reaction of Pentafluoriodobenzene and Ethylene with Dichlorine Heptoxide. By the above procedure, equimolar amounts of ethylene, pentafluoriodobenzene and dichlorine heptoxide gave ethylene diperchlorate (17%), 2-chloroethyl perchlorate (23%), pentafluoriodobenzene (87%) and ethyl perchlorate (5%).

Reaction of Trifluoroethyl Iodide and 1,1-Difluoroethylene
with Dichlorine Heptoxide. By the above procedure equimolar amounts of
trifluoroethyl iodide, 1,1-difluoroethylene and dichlorine heptoxide
gave 2-chloro-1,1-difluoroethyl perchlorate (31%), trifluoroethyl iodide
(37%), 1,1-difluoroethyl perchlorate (7%) and 2-iodo-1,1-difluoroethyl
perchlorate (3%). These perchlorates were identified by comparison with
authentic samples described elsewhere in this report.

C. Reactions of Dichlorine Heptoxide-Halogen and Silver Perchlorate-Halogen Mixtures with Olefins.

Reaction of Dichlorine Heptoxide and Iodine with 1,1-Difluoroethylene. To a suspension-solution of 0.254 g (1.0 mmol) of iodine in 10 ml of carbon tetrachloride was added 3.3 ml of dichlorine heptoxide solution in carbon tetrachloride (1.0 mmol of Cl_2O_7) and the reaction mixture was stirred at room temperature for 18 hrs. All the iodine was consumed to give an orange solution and a white precipitate. The mixture was filtered and to the filtrate was added, by syringe, 22 ml (1.0 mmol) of 1,1-difluoroethylene. The mixture was allowed to stand at room temperature overnight. The solution was concentrated to 3 ml: proton nmr (CCl_4) δ 3.52 (t) and 4.08 (t); fluorine nmr ϕ 45.6 (t) and 73.4 (t). The two compounds in the mixture were identified as 1,1-difluoro-1,2-diiodoethane and 1,1-difluoro-2-iodoethyl perchlorate. An authentic sample of the diiodo compound was prepared by the addition of iodine to 1,1-difluoroethylene in carbon tetrachloride solution, proton nmr (CCl_4) δ 4.07 (t); fluorine nmr ϕ 45.8. For the identification of the perchlorate, see below.

Reaction of Dichlorine Heptoxide and Iodine Chloride with 1,1-Difluoroethylene. Iodine chloride (0.10 g, 0.6 mmol) in 1.0 ml of carbon tetrachloride was added with stirring to 2 ml of 0.3 M dichlorine heptoxide in carbon tetrachloride. The mixture became turbid and gradually deposited a pale yellow solid. After 2 hrs the iodine chloride was consumed and 15 ml (0.7 mmol) of 1,1-difluoroethylene was added with a syringe. The mixture was allowed to stand overnight: proton nmr (CCl_4) δ 3.54 (t) and 3.72 (t); fluorine nmr ϕ 73.9 (t) and 80.2 (t). The δ 3.54 and ϕ 73.9 compound comprised 70% of

the sample.

The solution was concentrated to ca 20% of its original volume and the two compounds were separated by glpc (5' x 1/4" column of 12% QFI on chrom W, 60-80 mesh at 65°, the flow 60 cc/min, injector 105°, detector 145°). Two peaks, retention times 4.5 and 13.5 mm, were observed. Weighed samples of the trapped compounds were analyzed for H and F by nmr using chlorobenzene and hexfluorobenzene, respectively, as internal standards. The lower retention time component was characterized as 1,1-difluoro-2-chloroethyl perchlorate: proton nmr (CCl_4) δ 3.72 (t, $J_{\text{HF}} = 9.5$ Hz); fluorine nmr ϕ 80.2 (t, $J_{\text{HF}} = 9.5$ Hz).

Anal. Calcd for $\text{C}_2\text{H}_2\text{F}_2\text{Cl}_2\text{O}_4$: H, 1.01; F, 19.1. Found: H, 1.33; F, 16.7.

The other component in the mixture was identified as 1,1-difluoro-2-iodoethyl perchlorate; proton nmr (CCl_4) δ 3.52 (t, $J_{\text{HF}} = 11.5$ Hz); fluorine nmr ϕ 80.1 (t, $J_{\text{HF}} = 12.0$ Hz).

Anal. Calcd for $\text{C}_2\text{H}_2\text{F}_2\text{IClO}_4$: H, 0.69; F, 13.1. Found: H, 0.73; F, 12.7.

Reaction of Dichlorine Heptoxide and Iodine with Ethylene. To a freshly prepared Cl_2O_7 - I_2 mixture from 0.254 g (1.0 mmol) of iodine and 1.0 mmol of dichlorine heptoxide in 5cc of carbon tetrachloride was added 50 ml of ethylene. A mildly exothermic reaction was complete in 5 min. Glpc showed two compounds identified as 1-chloro-2-iodoethane (major component) and 2-chloroethyl perchlorate by comparison with authentic samples. An authentic sample of 1-chloro-2-iodoethane was prepared by adding iodine chloride to ethylene at room temperature. The reaction was completed in 30 min: nmr (CCl_4)

83.56 (m). Identification of 2-iodoethyl perchlorate is described below for the reaction product of AgClO_4 , I_2 and ethylene. Spectral and glpc properties were identical.

Reaction of Dichlorine Heptoxide and Chlorine with Ethylene. To 2 ml of 0.3 M dichlorine heptoxide solution in carbon tetrachloride was added 15 ml of chlorine and the mixture was allowed to stand at room temperature overnight. Ethylene (20 ml) was added by syringe and the mixture allowed to stand at room temperature overnight. The mixture was washed with water and dried. The nmr spectrum showed two compounds, 1,2-dichloroethylene and 2-chloroethyl perchlorate, compared with authentic samples. A sample of the perchlorate [proton nmr: δ 3.77 (t) and 4.66 (t)] was prepared from 2-chloroethanol and dichlorine heptoxide.

Reaction of Dichlorine Heptoxide and Bromine with Ethylene. An excess of ethylene was added to a mixture prepared by adding 0.096 g (0.6 mmol) of bromine in 1 ml of carbon tetrachloride to 2 ml of 0.3 M dichlorine heptoxide in carbon tetrachloride. The bromine color was discharged in 2 hrs. Nmr showed a mixture of 1,2-dichloromethane and 2-bromoethyl perchlorate in approximately equal amounts. 2-Bromoethyl perchlorate was prepared from 2-bromoethanol and dichlorine heptoxide: nmr (CCl_4), δ 3.52 (t) and 4.71 (t).

Reaction of Dichlorine Heptoxide and Chlorine with 1,1-Difluoroethylene. To a stirred solution of dichlorine heptoxide (1.0 mmol) in 3.3 ml of carbon tetrachloride was added 22 ml of chlorine and the flask was attached to a syringe containing 1,1-difluoroethylene. The reaction was allowed to proceed overnight. Nmr showed 1,2-dichloro-1,1-difluoroethane, 1,1-difluoroethyl perchlorate, and 2-chloro-1,1-difluoroethyl perchlorate (major product,

ca 50% yield). An authentic sample of 1,2-dichloro-1,1-difluoroethane was prepared by reacting 1,1-difluoroethylene with chlorine in carbon tetrachloride for 18 hrs: proton nmr (CCl_4) δ 3.92 (t); fluorine nmr ϕ 59.0 (t). 1,1-Difluoroethyl perchlorate, obtained by addition of perchloric acid to 1,1-difluoroethylene, is described above.

The composition of the mixture was further confirmed by gas chromatography by comparing retention times with those of authentic compounds. On a 5' x 1/4" 12% QF1 on chrom W, 60-80 mesh, column of 60° and He flow 60 cc/min, the retention times (min) were: 1,2-dichloro-1,1-difluoroethane 1, 1,1-difluoroethyl perchlorate 2, and 2-chloro-1,1-difluoroethyl perchlorate 4.

Reaction of Dichlorine Heptoxide and Iodine with Tetrafluoroethylene. A mixture of 0.254 g (1.0 mmol) of iodine and dichlorine heptoxide (1.0 mmol) in 7 ml of carbon tetrachloride was stirred at room temperature until the iodine was consumed to give a pale yellow mixture. The reaction flask was attached to a syringe containing tetrafluoroethylene and the reaction was allowed to proceed for 3 days. The mixture was washed with 5% aqueous sodium thiosulfate and with water and was dried over magnesium sulfate. The filtered solution was examined by fluorine nmr and exhibited several signals. The two strongest signals, triplets, at ϕ 72.8 ($J_{\text{FF}} = 4.5$ Hz) and 92.6 ($J_{\text{FF}} = 5.5$ Hz) were assigned to 2-chlorotetrafluoroethyl perchlorate, reported¹⁹ values: ϕ 72.7 and 92.5. This material was removed when the solution was concentrated to 1/3 of its original volume. The concentrate showed only two triplets, ϕ 63.4, $J_{\text{FF}} = 4.5$ Hz, and 90.2, $J_{\text{FF}} = 5.5$ Hz, which agree with the values assigned to 2-iodotetrafluoroethyl perchlorate¹².

The two weak triplets of δ 60.0 and 67.1, with somewhat longer coupling constants than those of the perchlorates, were assigned to 1-chloro-2-iodotetrafluoroethylene. An authentic sample of this compound was obtained by reacting tetrafluoroethylene with iodine chloride in carbon tetrachloride overnight: fluorine nmr (CCl_4) δ 59.8 ($J_{\text{FF}} = 8 \text{ Hz}$) and 66.9 ($J_{\text{HF}} = 8 \text{ Hz}$). A very weak singlet at δ 71.0 was assigned to 1,2-dichlorotetrafluoroethylene and that at 52.8 to 1,2-diiodotetrafluoroethylene. Authentic samples of these two halocarbons were obtained by adding chlorine or iodine to tetrafluoroethylene.

Yields of the above products, determined by nmr using hexafluorobenzene as the internal standard, were: 65, 15, 10, 5, and 5% for 2-chlorotetrafluoroethyl perchlorate, 2-iodotetrafluoroethyl perchlorate, 1-chloro-2-iodotetrafluoroethane, 1,2-diiodotetrafluoroethane, and 1,2-dichlorotetrafluoroethane, respectively.

In another experiment, 3.3 ml of a 0.3 M carbon tetrachloride solution of dichlorine heptoxide was added to a stirred suspension of 0.254 g (1.0 mmol) of iodine in 1.5 ml of carbon tetrachloride and the flask was attached to a syringe containing tetrafluoroethylene. The reaction was completed in 4 hrs at room temperature. The reaction products, 2-chlorotetrafluoroethyl perchlorate, 2-iodotetrafluoroethyl perchlorate, 1-chloro-2-iodotetrafluoroethane, 1,2-diiodotetrafluoroethane, and 1,2-dichlorotetrafluoroethane, were obtained in 15, 30, 20, 25, and 5% yields, respectively.

Reaction of Dichlorine Heptoxide and Iodine Chloride with Tetrafluoroethylene. The reaction of $\text{Cl}_2\text{O}_7\text{-ICl}$ and tetrafluoroethylene was carried out employing the same conditions described above for the analogous reaction

of iodine. The reaction, completed in 4 hrs, yielded 2-chlorotetrafluoroethyl perchlorate, 1-chloro-2-iodotetrafluoroethane, and 1,2-dichlorotetrafluoroethane in 50, 35, and 15% yields, respectively.

Reaction of Dichlorine Heptoxide and Iodine Bromide with Tetrafluoroethylene. By the above procedure, dichlorine heptoxide and iodine bromide reacted with tetrafluoroethylene (1.5 hrs) to give a mixture of 2-bromotetrafluoroethyl perchlorate, 2-iodotetrafluoroethyl perchlorate, and 1-bromo-2-iodotetrafluoroethane in 40, 35, and 5% yields, respectively. The identification of 2-bromotetrafluoroethyl perchlorate is tentative and is based on the analogy between its nmr spectra (fluorine nmr: δ 67.9 (t, $J_{HF} = 4.5$ Hz) and 91.8 (t, $J_{HF} = 5.0$ Hz) and those of 2-chloro- and 2-iodotetrafluoroethyl perchlorates. An authentic sample of 1-bromo-2-iodotetrafluoroethane was obtained by adding iodine bromide to tetrafluoroethylene; fluorine nmr (CCl_4): δ 56.6 (t) and 59.9 (t).

Reaction of Silver Perchlorate and Chlorine with 1,1-Difluoroethylene. To a stirred suspension of 0.207 g (1.0 mmol) of anhydrous silver perchlorate in 5 ml of carbon tetrachloride was added 25 ml of chlorine and the reactor was attached to a syringe containing 1,1-difluoroethylene. The reaction was completed in 1.5 hrs. Proton and fluorine nmr spectra showed that the product of this reaction was 2-chloro-1,1-difluoroethyl perchlorate (95%).

Reaction of Silver Perchlorate and Bromine with 1,1-Difluoroethylene. By the above procedure silver perchlorate and bromine were reacted with 1,1-difluoroethylene (reaction time, 10 min) to give a 98% yield of 2-bromo-1,1-difluoroethyl perchlorate: proton nmr (CCl_4) δ 3.60 (t); fluorine

nmr δ 77.4 (t). The product contained trace amounts of 1,2-dibromo-1,1-difluoroethane, a reference sample of which was prepared by the addition of bromine to 1,1-difluoroethylene (reaction time, 1 hr): proton nmr (CCl_4) δ 3.95 (t, $J_{\text{HF}} = 12.5$ Hz); fluorine nmr δ 50.4 (t, $J_{\text{HF}} = 12.3$ Hz).

Reaction of Silver Perchlorate and Iodine with 1,1-Difluoroethylene. By the above procedure silver perchlorate and iodine were reacted with 1,1-difluoroethylene (1.5 hrs) to give 2-iodo-1,1-difluoroethyl perchlorate in 98% yield.

Reaction of Silver Perchlorate and Iodine Chloride with 1,1-Difluoroethylene. Silver perchlorate and iodine chloride were reacted with 1,1-difluoroethylene (1-2 min) as above to give a mixture of 2-iodo-1,1-difluoroethyl perchlorate (60%) and 1-chloro-2-iodo-1,1-difluoroethane (40%).

Reaction of Silver Perchlorate and Iodine Bromide with 1,1-Difluoroethylene. To a suspension of 0.207 g (1.0 mmol) of anhydrous silver perchlorate in 1 ml of carbon tetrachloride was added a solution of 0.207 g (1.0 mmol) of iodine bromide in 5 ml of carbon tetrachloride and the mixture was stirred at room temperature for 18 hrs. To the mixture was added 1,1-difluoroethylene and the reaction was allowed to proceed until the dark color of iodine bromide was completely bleached (2.5 hrs). The clear and colorless solution contained 2-iodo-1,1-difluoroethyl perchlorate as the sole reaction product in a practically quantitative yield.

Reaction of Silver Perchlorate and Iodine with Ethylene. To a solution-suspension of 0.253 g (1.0 mmol) of iodine in 5 ml of carbon tetrachloride was added 0.207 g (1.0 mmol) of anhydrous silver perchlorate and ethylene was added with stirring until the iodine was consumed (30 min).

The colorless solution was decanted from the silver salts: nmr (CCl_4) δ 3.33 (t), $-\text{CH}_2\text{OCClO}_3$, 4.68 (t), and 3.60 (s). The first two signals were assigned to 2-iodoethyl perchlorate and the 3.60 signal to 1,2-diiodoethane. The two compounds were present in approximately equal amounts.

Reaction of Silver Perchlorate and Iodine Chloride with Ethylene.

By the above procedure, anhydrous silver perchlorate and iodine chloride were reacted with ethylene to give a mixture of 2-iodoethyl perchlorate (ca 20%) and 1-chloro-2-iodoethane (ca 30%).

Reaction of Silver Perchlorate and Iodine Bromide with Ethylene.

By the above procedure, 2-iodoethyl perchlorate (nmr triplets of δ 3.49 and 4.69) was obtained in 85% yield by reacting silver perchlorate and iodine bromide with ethylene (10 min). Trace amounts of 1-bromo-2-iodoethane (nmr δ 3.57), also prepared by the addition of iodine bromide to ethylene, were present in the solution.

Reaction of Silver Perchlorate and Iodine Chloride with Tetrafluoroethylene. To a suspension of 0.207 g (1.0 mmol) of anhydrous silver perchlorate in 5 ml of carbon tetrachloride was added 0.162 g (1.0 mmol) of iodine chloride and the flask was connected to a syringe containing tetrafluoroethylene. The reaction mixture, was stirred at room temperature overnight and filtered: fluorine nmr (CCl_4): δ 63.4 (t) and 90.2 (t) assigned to 2-iodotetrafluoroethyl perchlorate, 85% yield (determined by nmr using hexafluorobenzene as a standard).

Reaction of Silver Perchlorate and Chlorine with 1,1-Dichloroethylene. To a stirred suspension of 0.207 g (1.0 mmol) of anhydrous silver perchlorate in 5 ml of carbon tetrachloride was added 22 ml of chlorine and

0.120 g (1.2 mmol) of 1,1-dichloroethylene and the reaction was allowed to proceed for 1.5 hrs. The colorless solution was decanted from the silver chloride: nmr δ 4.2 (s) and 4.10 (s). The δ 4.21 signal was due to 1,1,1,2-tetrachloroethane; an authentic sample was prepared by the addition of chlorine to the olefin. The other signal was assigned to 1,1,2-trichloroethyl perchlorate.

Reaction of Silver Perchlorate and Bromine with 1,1-Dichloroethylene. By the above procedure, silver perchlorate and bromine reacted with 1,1-dichloroethylene to give approximately equal molar mixture of 1,1,1,2-tetrabromoethane (δ 4.32) and 1,1-dichloro-2-bromoethyl perchlorate (δ 4.05).

Reaction of Silver Perchlorate and Iodine with 1,1-Dichloroethylene. By the above procedure, silver perchlorate and iodine reacted with 1,1-dichloroethylene (4 hrs) to give a single product which was tentatively characterized as 1,1-dichloro-2-iodoethyl perchlorate; nmr (CCl_4) δ 4.17 (s).

Reaction of Silver Perchlorate and Iodine Chloride with 1,1-Dichloroethylene. By the above procedure, silver perchlorate and iodine chloride reacted with 1,1-dichloroethylene to give 1,1-dichloro-2-iodoethyl perchlorate as the sole reaction product. The reaction was completed in 5 min.

D. Miscellaneous Reactions.

Reactions of Olefins with Perchloric Acid. Water (0.0080 g, 0.44 mmol) was stirred with 2 ml of 0.3 M dichlorine heptoxide for 30 min in a 25 ml flask. The flask was evacuated partially and 13.4 ml (0.6 mmol) of 1,1-difluoroethylene was added by syringe. In 2 hrs, the solution was washed with water and dried over sodium sulfate. Nmr analysis using chlorobenzene as a quantitative reference showed only 1,1-difluoroethyl perchlorate, obtained in 76% yield: proton nmr (CCl_4) δ 1.95 ppm (t, $J = 14$ Hz); fluorine nmr ϕ 69.52 (q, $J = 14$ Hz); ir (CCl_4) 1390 (m), 1280 (vs), 1200 (s), 1150 (s), 1130 (s), 1030 (s), 970 (s) and 920 cm^{-1} (s).

The reaction of propene with perchloric acid by the above procedure gave, after 24 hrs, a 65% yield of isopropyl perchlorate and a 10% yield of 1-chloro-2-propyl perchlorate identical with an authentic sample⁷.

Allyl chloride gave a 91% yield of 1-chloro-2-propyl perchlorate in 24 hrs by this procedure.

Ethylene by this procedure gave a 63% yield of ethyl perchlorate.

1,1-Dichloroethylene gave no reaction in 24 hrs under these conditions.

Reaction of Aldehydes with Dichlorine Heptoxide. Valeraldehyde (0.0516 g, 0.6 mmol) was added with stirring to 2 ml of 0.6 M dichlorine heptoxide in carbon tetrachloride. An orange oil separated immediately and the nmr spectrum of the carbon tetrachloride layer showed no signals. The mixture was stirred with water and the carbon tetrachloride layer was dried over magnesium sulfate. Nmr analysis showed an 86% yield of valeric acid, identified by ir and glpc comparison with an authentic sample.

By the same procedure, nonanaldehyde gave an 83% yield of nonanoic acid.

Pivaldehyde (0.052 g, 0.6 mmol) was added to 2 mol of 0.3 M dichlorine heptoxide in carbon tetrachloride with stirring. The progress of the reaction was followed by nmr. After 10 min the -CHO hydrogen (δ 9.67) began to disappear and new singlets were formed at δ 6.13 and 1.50 in a ratio of 1:9. Then a separate liquid phase began to form, and in 40 min no nmr signals were observed in the carbon tetrachloride layer. The insoluble liquid was identified by nmr, ir and glpc as pivalic acid (81% yield).

Reaction of 2-Iodotetrafluoroethyl Perchlorate with Hexylamine.

Tetrafluoroethylene (46 ml, 2 mmol) was added by syringe to a stirred slurry of 0.415 g (2 mmol) of silver perchlorate, 0.325 g (2 mmol) of iodine chloride and 15 ml of 1,1,3-trichlorotrifluoroethane in a partially evacuated flask at room temperature. In 3 hrs the reaction mixture was washed with water and with 5% sodium thiosulfate, and the solution was dried over magnesium sulfate. Nmr analysis (benzotrifluoride as quantitative standard) showed an 83% yield of 2-iodotetrafluoroethyl perchlorate: δ 89.92 (t, $J = 4$ Hz, 2 F, $\text{CF}_2\text{OCClO}_3$) and 69.92 ppm (t, $J = 4$ Hz, 2 F, CF_2I).

Hexylamine (0.404 g, 4 mmol) in 5 ml of 1,1,2-trichlorotrifluoroethane was added dropwise, with stirring at 0° to a solution of 2 mmol of 2-iodotetrafluoroethyl perchlorate in 10 ml of 1,1,2-trichlorotrifluoroethane. An immediate reaction took place and white solids separated. After 30 min. the mixture was washed with dilute hydrochloric acid and with water. The organic layer was extracted with 0.01 N sodium hydroxide solution, and the latter was acidified with 0.01 N hydrochloric acid and extracted with carbon

tetrachloride. Nmr and ir spectra of the carbon tetrachloride solution showed a 27% yield of N-perchlorylhexylamine, identical with an authentic sample (Appendix B). The 1,1,2-trichlorotrifluoroethane solution was washed with water and with 5% sodium thiosulfate solution and was dried over magnesium sulfate. Fluorine nmr showed 2-iodotetrafluoroethyl perchlorate (12% recovery) and N-hexyl-1,1-difluoro-1-iodoacetamide (33%). The latter was isolated by column chromatography on neutral activated alumina: proton nmr (CCl_4) δ 6.63 (broad s, 1 H, NH, exchanged with D_2O), 3.23 (q, $J = 6$ Hz, NHCH_2CH_2), 1.38 (m, 8 H, CH_2) and 0.90 ppm (m, 3 H, CH_3); fluorine nmr (CCl_4) δ 56.28 (s, CF_2); ir (CCl_4) 3450 (NH), 1715 ($\text{C}=\text{O}$), 1200, 1170, and 1120 cm^{-1} (CF).

Anal. Calcd for $\text{C}_8\text{H}_{14}\text{NF}_2\text{OI}$: C, 31.5; H, 4.6; N, 4.6; I, 41.6.
 Found: C, 30.53 H, 4.26; N, 4.01; I, 38.78.

REFERENCES

1. J. Radell, J.W. Connolly and A.J. Raymond, J. Amer. Chem. Soc., 83, 3958 (1961).
2. L.F. Fieser and W. von E. Doering, J. Amer. Chem. Soc., 68, 2252 (1946).
3. A.F. Ferris, K.J. McLean, I.C. Marks and W.D. Emmons, J. Amer. Chem. Soc., 75, 4078 (1953).
4. N. Kornblum, W.J. Jones, and G. J. Anderson, J. Amer. Chem. Soc., 81, 4113 (1959).
5. N. Kornblum and H.E. Ungnade, Org. Syn., Coll. Vol., 4, 724 (1963).
6. C.D. Beard, K. Baum and V. Grakauskas, J. Org. Chem., 38, 3673 (1973).
7. Fluorochem, Inc., Report ONR 1-2, January 1973.
8. J. Thiele and W. Peter, Ber., 38, 2842 (1905); Ann., 369, 119 (1909).
9. C. Walling and J.A. McGuinness, J. Amer. Chem. Soc., 91, 2053 (1969).
10. A. Michael and W.T. Conn, J. Amer. Chem. Soc., 23, 100 (1900).
11. C.J. Shack and D. Pilipovich, J. Inorg. Chem., 12, 897 (1973).
12. C.J. Shack and D. Pilipovich, Abstracts of 7th International Symposium on Fluorine Chemistry, Santa Cruz, California, July 15-20, 1973, P25.
13. For a review see N.W. Alcock and T.C. Waddington, J. Chem. Soc., 1962, 2510
14. Gomberg, J. Amer. Chem. Soc., 45, 398 (1923).
15. K.O. Christe and C.J. Shack, Inorg. Chem. 11, 1682 (1972).
16. The solubility of silver perchlorate in benzene at 25° is 45.29 g/l:
A.J. Hill, J. Amer. Chem. Soc., 43, 254 (1921).

17. G. Cady, Inorg. Synth., 5, 156 (1957).
18. K. Baum, J. Amer. Chem. Soc., 92, 2927 (1970).
19. C.J. Shack, D. Pilipovich, and J.F. How, Inorg. Chem., 12, 897 (1973).

Reactions of Dichlorine Heptoxide with Alcohols

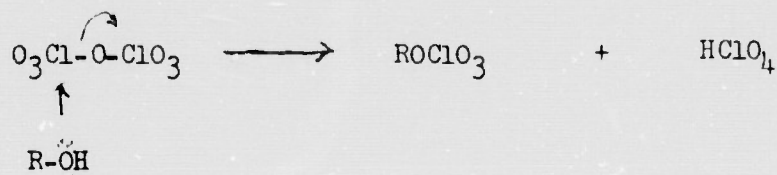
Kurt Baum and Charles D. Beard

Contribution from Fluorochem Inc., Azusa, California 91702

Abstract: Dichlorine heptoxide in carbon tetrachloride is a general reagent for converting alcohols to alkyl perchlorates. Simple primary alcohols, as well as ethylene glycol, 1,4-butanediol, 2,2,2-trifluoroethanol, 2,2-dinitropropanol, 2-fluoro-2,2-dinitroethanol, 2-(2-fluoro-2,2-dinitroethoxy)-ethanol, allyl alcohol and propargyl alcohol gave corresponding unrearranged perchlorates. Isopropanol gave isopropyl perchlorate. 2-Hexanol and 3-hexanol gave mainly the unrearranged perchlorates, with the corresponding ketones, and in the latter case, the isomeric secondary perchlorate as byproducts. The sodium salts of perfluoro-t-butanol, 1,1,1,3,3,3-hexafluoro-2-phenyl-2-propanol and 1,1,1,3,3,3-hexafluoro-2-methyl-2-propanol gave the corresponding tertiary perchlorates. The perchlorates, obtained as carbon tetrachloride solutions, could be used directly as alkylating agents. Lithium bromide with 1,4-butanediperchlorate, 1,2-ethanediperchlorate, pentyl perchlorate and propargyl perchlorate gave the corresponding bromides. Ethers were prepared by the reactions of pentyl perchlorate with pentanol, isopropyl perchlorate with pentanol and allyl perchlorate with 2-fluoro-2,2-dinitroethanol. Hexyl perchlorate and dimethyl sulfoxide gave hexaldehyde.

The synthesis of dichlorine heptoxide was first reported by Michael and Conn in 1900 by the reaction of perchloric acid with phosphorous pentoxide.² Several variations of this method were reported³⁻⁷ and the physical^{4,5,7,8} and spectroscopic⁹⁻¹² properties of dichlorine heptoxide were studied extensively. However, the chemical properties of this compound, the anhydride of perchloric acid, are virtually unexplored. The present paper deals with reactions of dichlorine heptoxide with alcohols, and its reactions with other organic and inorganic groups will be described subsequently.

Nucleophilic attack by an alcohol on chlorine in dichlorine heptoxide would yield an alkyl perchlorate. The carbon-oxygen bond is not ruptured in this reaction, and in contrast to previously reported perchlorate syntheses, a carbonium ion intermediated is not involved.



Although methyl perchlorate and ethyl perchlorate have been prepared by several methods¹³, there is no selective method available for higher aliphatic perchlorates.^{14, 15} Because of the low nucleophilicity of the perchlorate ion,^{16,17} competing rearrangements could be expected in its reactions with carbonium ions or incipient carbonium ions.

Because of the miscibility of dichlorine heptoxide with carbon tetrachloride and the close proximity of the boiling points of the two liquids,³ a carbon tetrachloride solution of dichlorine heptoxide is a safe and convenient preparative reagent. The reagent used in this work was prepared

by adding 70% perchloric acid to a suspension of phosphorous pentoxide in carbon tetrachloride, heating under reflux and then vacuum distilling the solution.

Primary Alcohols. The generality of the synthesis of perchlorates by the reaction of primary alcohols with dichlorine heptoxide is shown by the examples in Table I. Nmr spectra showed that the products were obtained in high purity and secondary perchlorate isomers were clearly absent. This reaction thus provides a convenient source of simple primary alkyl perchlorates. The reaction was also applied to two α,ω -diols, ethylene glycol and 1,4-butanediol, to give the corresponding diperchlorates. Alcohols with electron withdrawing substituents likewise reacted with dichlorine heptoxide; 2,2,2-trifluoroethanol, 2,2-dinitropropanol, 2-fluoro-2,2-dinitroethanol and 2-(2-fluoro-2,2-dinitroethoxy)ethanol were converted to the corresponding perchlorates. Even unsaturated alcohols were found to be amenable to this reaction, and allyl perchlorate and propargyl perchlorate were prepared from allyl alcohol and propargyl alcohol, respectively. Unsuccessful attempts to prepare allyl perchlorate have been reported.¹⁸

Simple alkyl perchlorates were prepared by treating the alcohol with the theoretical amount of 0.3 M solution of dichlorine heptoxide in carbon tetrachloride for 18 hrs. Longer reaction times were generally used with electronegatively substituted alcohols, and in some cases methylene chloride was added to enhance solubility. The unsaturated alcohols were treated with the reagent for 0.5 hr at 0°. Side reactions due to the reaction liberated perchloric acid with the

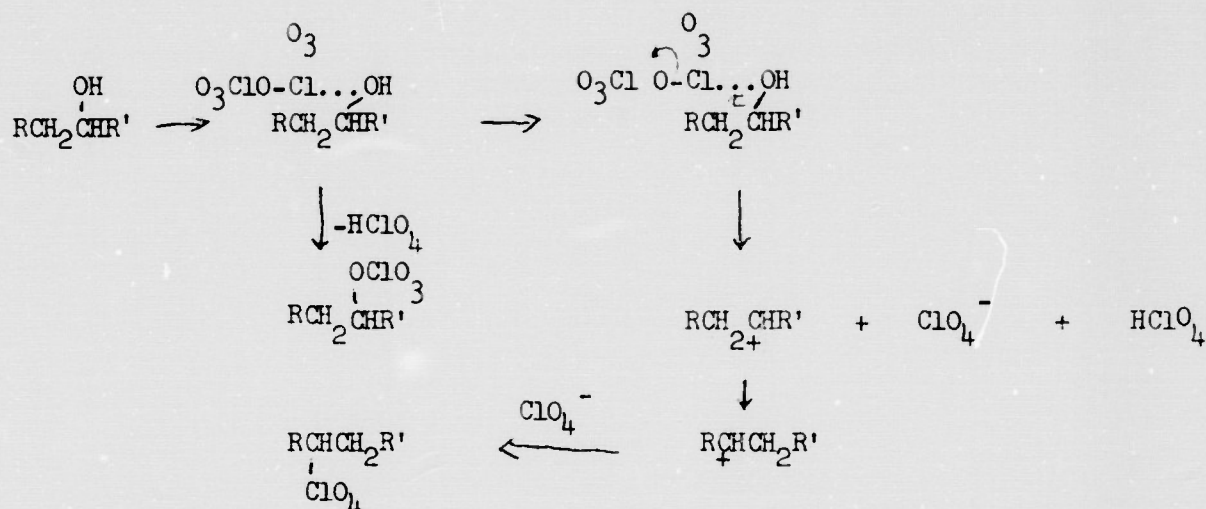
Table I. Primary Perchlorates

<u>Starting Material</u>	<u>Product</u>	<u>Yield(%)</u>
CH_3OH	CH_3OClO_3	42
$\text{C}_2\text{H}_5\text{OH}$	$\text{C}_2\text{H}_5\text{OClO}_3$	56
$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{OClO}_3$	73
$\text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{OH}$	$\text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{OClO}_3$	71
$\text{CH}_3(\text{CH}_2)_3\text{CH}_2\text{OH}$	$\text{CH}_3(\text{CH}_2)_3\text{CH}_2\text{OClO}_3$	63
$\text{CH}_3(\text{CH}_2)_4\text{CH}_2\text{OH}$	$\text{CH}_3(\text{CH}_2)_4\text{CH}_2\text{OClO}_3$	58
$\text{HOCH}_2\text{CH}_2\text{OH}$	$\text{ClO}_3\text{OCH}_2\text{CH}_2\text{OClO}_3$	60
$\text{HOCH}_2(\text{CH}_2)_2\text{CH}_2\text{OH}$	$\text{ClO}_3\text{OCH}_2(\text{CH}_2)_2\text{CH}_2\text{OClO}_3$	38
$\text{CF}_3\text{CH}_2\text{OH}$	$\text{CF}_3\text{CH}_2\text{OClO}_3$	55
$\text{CH}_3\text{C}(\text{NO}_2)_2\text{CH}_2\text{OH}$	$\text{CH}_3\text{C}(\text{NO}_2)_2\text{CH}_2\text{OClO}_3$	67
$\text{FC}(\text{NO}_2)_2\text{CH}_2\text{OH}$	$\text{FC}(\text{NO}_2)_2\text{CH}_2\text{OClO}_3$	60
$\text{FC}(\text{NO}_2)_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$	$\text{FC}(\text{NO}_2)_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OClO}_3$	43
$\text{CH}_2=\text{CHCH}_2\text{OH}$	$\text{CH}_2=\text{CHCH}_2\text{OClO}_3$	48
$\text{HC}\equiv\text{CCH}_2\text{OH}$	$\text{HC}\equiv\text{CCH}_2\text{OClO}_3$	43

double and triple bonds were prevented by adding sodium sulfate to the reaction mixtures to adsorb the acid.

Secondary Alcohols. Isopropyl perchlorate was obtained in 48% yield from isopropanol and dichlorine heptoxide by following the general procedure used for simple primary alcohols. 2-Hexanol and 3-hexanol gave 2-hexyl perchlorate and 3-hexyl perchlorate in yields of 62% and 53%, respectively. Some oxidation, and, at least in the latter case, some rearrangement was also observed. Thus, in the 2-hexanol reaction, 2-hexanone was obtained in 8% yield. No 3-hexyl perchlorate was observed, but the limit of detection by nmr is about 10% because of overlapping peaks of the two perchlorates. In the 3-hexanol reaction, a 9% yield of 3-hexanone was obtained, as well as a 6% yield of 2-hexyl perchlorate, which is readily observed by its methyl doublet at δ 1.48. The perchlorates did not interconvert under the reaction conditions.

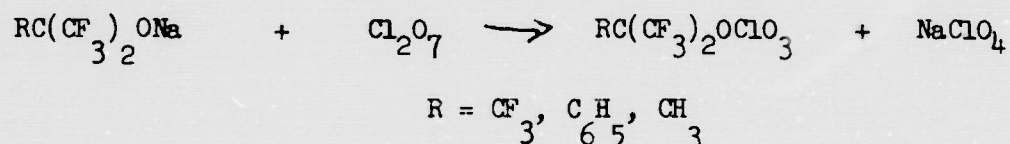
The oxidation of the alcohols to ketones could take place through cyclic complexes similar to those that have been postulated for chromate oxidations^{19,20}. The formation of isomeric perchlorates suggest that the initial alcohol complex undergoes carbon-oxygen bond cleavage in competition with the loss of perchloric acid. Hydride shift in the resulting carbonium ion or incipient carbonium ion or elimination-addition would lead to the isomeric perchlorate.



Tertiary Alcohols. Tertiary perchlorates have not been reported previously, other than trityl derivatives, which have properties of carbonium ion salts²¹. The covalent character of tertiary perchlorates would be expected to increase with the degree of electron-withdrawing substitution. The reactivity of tertiary alcohols toward dichlorine heptoxide, however, would decrease with electron - withdrawing substituents, and steric hinderance would also reduce their reactivity.

t-Butanol was found to react on mixing with dichlorine heptoxide in carbon tetrachloride, but a complex intractable mixture was obtained. Three fluorine-substituted tertiary alcohols were also examined, perfluoro-t-butanol, 1,1,1,3,3,3-hexafluoro-2-phenyl-2-propanol and 1,1,1,3,3,3-hexafluoro-2-methyl-2-propanol. These alcohols did not give perchlorates with dichlorine heptoxide within several days. The alkoxides, however, readily gave the corresponding perchlorates. The fluorine nmr spectra of the crude carbon tetrachloride solutions showed only the perchlorates and the starting alcohols.

The alcohols were removed from the solutions by washing with 1N sodium hydroxide without affecting the perchlorates. The phenyl derivative was isolated by preparative glpc and the others, which could not readily be separated from the solvent were characterized spectrally.

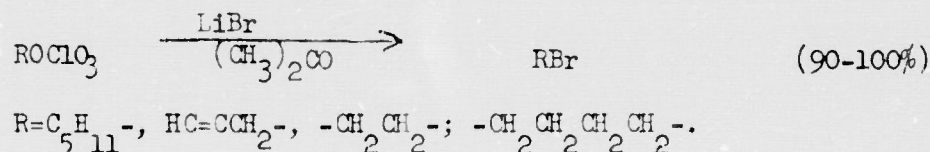


Characterization and Reactions of Perchlorates. The dichlorine heptoxide-alcohol reaction provides alkyl perchlorates as insensitive solutions in carbon tetrachloride. They can be utilized as chemical reagents in this form without the necessity of handling the neat materials, which are generally sensitive explosives. Two examples, 2,2-dinitropropyl perchlorate and 2-fluoro-2,2-dinitroethyl perchlorate, were isolated by vacuum transfer and combustion analyses were obtained. A procedure requiring less tedious manipulation was used with 1,1,1,3,3,3-hexafluoro-2-phenyl-2-propyl perchlorate; a weighed sample, isolated by glpc, was diluted with solvent and analyzed for H and F by nmr integration against quantitative reference standards. The structural assignment of allyl perchlorate was confirmed by an alternative synthesis from allyl bromide, and silver perchlorate in carbon tetrachloride.

Nmr and ir spectra of the perchlorates are described in the Experimental Section. Nmr chemical shifts and coupling data, as well as areas ratios are in agreement with the structures. It is noteworthy that hydrogens on the carbon atoms bearing a perchlorate group were consistently deshielded by 0.7 to 1.0 ppm relative to the corresponding hydrogens of the starting alcohols.

The ir spectra show characteristic perchlorate bands. Perhaloalkyl perchlorate bands at 1295 - 1320 (doublet) and 997-1036 cm^{-1} have been assigned to the Cl=O antisymmetric and symmetric stretching vibrations, respectively²². The observed spectra show strong bands in these regions, with shifts to lower frequency for substrates not as highly electron-withdrawing. Bands in the C-O stretch region are also apparent.

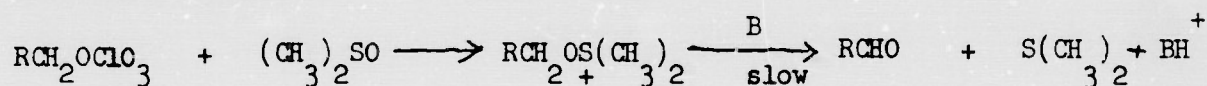
Some reactions utilizing alkyl perchlorates in carbon tetrachloride were investigated to provide additional structure proof as well as to demonstrate synthetic utility of the reagents. Mixing the carbon tetrachloride solutions with a 10% solution of lithium bromide in acetone gave the corresponding bromides in yields of 90-100%. Pentyl perchlorate, propargyl perchlorate, 1,2-ethane-diperchlorate and 1,4-butanediperchlorate were used in this reaction.



Solutions of perchlorates in carbon tetrachloride, as obtained from the dichlorine heptoxide reaction, can be used directly as alkylating agents for the preparation of ethers under mild conditions. Thus, pentyl perchlorate and pentanol in the persence of potassium carbonate gave 90% yield of dipentyl ether in 8 days at room temperature. Similarly, isopropyl perchlorate and pentanol gave an 85% yield of isopropyl pentyl ether in 6 days, with sodium sulfate used to adsorb liberated perchloric acid. Allyl perchlorate and 2-fluoro-2,2-dinitroethanol in the presence of potassium carbonate gave a 79% yield of allyl 2-fluoro-2,2-dinitroethyl ether in 48 hrs. This reaction constitutes a versatile synthetic procedure for the preparation of ethers under neutral or mildly basic conditions in a nonpolar solvent.



The perchlorate reagents can also be used for the preparation of aldehydes using dimethyl sulfoxide. A solution of hexyl perchlorate in carbon tetrachloride was treated with dimethyl sulfoxide and sodium bicarbonate. An initially exothermic reaction took place with complete consumption of the perchlorate followed by the slow formation of hexaldehyde, with a 95% yield in 24 hrs. The reaction parallels that of hexyl 4-nitrobenzenesulfonate ²³.



Although a few organic perchlorates have been known for many years, the utilization of this class of compounds has been hampered by the lack of selective and safe synthetic methods. The reaction of alcohols with dichlorine heptoxide in carbon tetrachloride provides the first general route to primary, secondary and tertiary perchlorates. The solutions obtained can be used directly as synthetic reagents.

Experimental Section

Proton and fluorine nmr spectra were recorded with a Varian T-60 spectrometer, and ir spectra were recorded with a Perkin-Elmer 700 Spectrometer. A varian 920 chromatograph with a 5 ft x 0.25 in column of 12 % QF-1 on Chromosorb W was used for glpc separations.

Alkyl perchlorates are generally sensitive explosives, and the neat materials should be handled only with adequate protective devices.

Dichlorine Heptoxide. To a suspension of 50 g (0.35 mol) of phosphorous pentoxide in 100 ml of carbon tetrachloride, 5.1 ml (0.0603 mol) of 70 % perchloric acid was added dropwise with stirring over a 2 hr period. The mixture was cooled with an ice bath during the addition. The bath was removed and stirring was continued for 2 hrs. The mixture was then heated under reflux for 1.5 hrs. The phosphorous pentoxide gradually became a sponge-like mass and stirring was then discontinued. The mixture was cooled to room temperature and the carbon tetrachloride and dichlorine heptoxide were co-distilled into a dry-ice-cooled receiver at 60-20mm. The distillate consisted of 93 ml (149 g) of a pale yellow liquid which was found to contain 0.30 mmol of dichlorine heptoxide per ml of solution (93% yield) by titration after stirring for 45 min with 1 N sodium hydroxide. The nmr spectrum showed no perchloric acid.

Although this procedure was repeated more than ten times without incident, the use of safety shielding is recommended. The same procedure was used to prepare a solution of dichlorine heptoxide in d-chloroform, a reagent useful for following, by nmr, reactions of alcohols with low solubility in carbon tetrachloride. Particular caution should be observed in extending the reaction to other solvents; explosions occurred during refluxing when ethylene dichloride or cyclohexane were used. It is

noteworthy that in these attempts, the characteristic swelling of the phosphorous pentoxide particles did not take place.

Reaction of Alcohols with Dichlorine Heptoxide, General Procedure.

The alcohol (0.6 mmol) was added to 2 ml of carbon tetrachloride solution of dichlorine heptoxide (0.6 mmol) at 0° with stirring. The mixture was stirred 18 hrs at room temperature, and then was washed with water and dried over magnesium sulfate. Yields were determined by nmr, using chlorobenzene as a quantitative internal standard.

Methyl Perchlorate. This compound was obtained in 42% yield. nmr (CCl_4) δ 4.22 ppm (s); ir (CCl_4) 1280 (vs), 1250 (vs), 1045 (s), 965 (s) and 700 cm^{-1} (s).

Ethyl Perchlorate. This compound was obtained in 56% yield: nmr (CCl_4) δ 4.57 (q, 2 H, $J = 6.5\text{ Hz}$, CH_2OClO_3) and 1.53 ppm (t, 3 H, $J = 6.5\text{ Hz}$, CH_3); ir (CCl_4) 1275 (vs), 1240 (vs), 1045 (s), 1000 (s), 880 (s), 720 cm^{-1} (s).

Propyl Perchlorate. This compound was obtained in 73% yield: nmr (CCl_4) δ 4.45 (t, 2 H, $J = 6\text{ Hz}$, CH_2OClO_3), 1.87 (septet, 2 H, CH_2), and 1.80 ppm (t, 3 H, $J = 7\text{ Hz}$, CH_3); ir (CCl_4) 1275 (vs), 1240 (vs), 1040 (s), 850 (s), 820 (s), 715 cm^{-1} (s).

Butyl Perchlorate. This compound was obtained in 71% yield: nmr (CCl_4) δ 4.40 (t, 2 H, $J = 6\text{ Hz}$, CH_2OClO_3), 2.19 (broad m, 4 H, CH_2CH_2), and 0.98 ppm (m, 3 H, CH_3); ir (CCl_4) 1280 (vs), 1140 (m), 1040 (s), 1240 (vs), 980 (m), 940 (s), 860 (m), 720 cm^{-1} (s).

Pentyl Perchlorate. This compound was obtained in 63% yield: nmr (CCl_4) δ 4.52 (t, 2 H, $J = 6.5\text{ Hz}$, CH_2OClO_3), 2.00 (m, 2 H, $\text{CH}_2\text{CH}_2\text{OClO}_3$),

1.45 (m, 4 H, CH_2), and 0.95 ppm (m, 3 H, CH_3); ir (CCl_4) 1280 (vs), 1245 (vs), 1140 (m), 1045 (s), 960 (s), 940 (m), 890 (s), 720 cm^{-1} (s).

Hexyl Perchlorate. This compound was obtained in 58% yield: nmr (CCl_4) δ 4.50 (t, 2 H, $J = 6\text{ Hz}$, CH_2OClO_3), 1.82 (m, 2 H, $-\text{CH}_2\text{CH}_2\text{OClO}_3$), 1.42 (m, 6 H, CH_2), and 0.92 ppm (m, 3 H, CH_3); ir (CCl_4) 1280 (vs), 1245 (vs), 1050 (s), 990 (m), 950 (s), 915 (s), 720 cm^{-1} (s).

1,2-Ethanediperchlorate. Ethylene glycol (0.0186 g, 0.3 mmol) was added to a solution of 0.6 mmol of dichlorine heptoxide in 4 ml of carbon tetrachloride and the mixture was stirred 18 hrs at ambient temperature. Nmr analysis, using chlorobenzene as a quantitative standard, showed a 60% yield of 1,2-ethanediperchlorate. In a larger scale reaction, 0.186 g (3 mmol) of ethylene glycol was added to a mixture of 20 ml of methylene chloride and 20 ml of a 0.3 M solution of dichlorine heptoxide in carbon tetrachloride. This homogeneous solution was stirred for 18 hrs at ambient temperature, washed with water, dried, and concentrated under vacuum to a volume of 2 ml. 1,2-Ethanediperchlorate was isolated by preparative glpc at 120° : nmr (CDCl_3) δ 4.83 ppm (s); ir (CDCl_3) 2990 (w), 1460 (w), 1285 (vs), 1250 (vs), 1060 (m), 1020 (s), and 980 cm^{-1} (m).

1,4-Butanediperchlorate. 1,4-Butanediol (0.054 g, 0.6 mmol) was added to 5 ml of 0.3 M dichlorine heptoxide in carbon tetrachloride and the mixture was stirred for 18 hrs at ambient temperature. The organic layer was washed with water and dried over magnesium sulfate. The yield of 1,4-butanediperchlorate was 38%: nmr (CCl_4) δ 4.60 (m, 4 H, $-\text{CH}_2\text{OClO}_3$) and 3.70 ppm (m, 4 H, CH_2CH_2); ir (CCl_4) 3000 (m), 1475 (m), 1460 (m), 1390 (w), 1280 (vs), 1245 (vs), 1045 (s), 930 (s), and 700 cm^{-1} (s).

2,2,2-Trifluoroethyl Perchlorate. 2,2,2-Trifluoroethanol (0.150 g, 1.5 mmol) was added to 5 ml 0.3 M dichlorine heptoxide in carbon tetrachloride at room temperature and the mixture was stirred for 48 hrs. The solution was washed with water and dried. The yield of 2,2,2-trifluoroethyl perchlorate was 55%: proton nmr (CCl_4) δ 4.80 (q, $J_{\text{HF}}=8$ Hz); fluorine nmr (CCl_4) δ + 91 ppm (t, $J_{\text{HF}}=8$ Hz); ir (CCl_4) 1440 (w), 1400 (m), 1280 (vs), 1245 (vs), 1180 (vs), 1030 (s), 1005 (s), 985 (m), and 860 cm^{-1} (m).

2,2-Dinitropropyl Perchlorate. 2,2-Dinitropropanol (0.45 g, 3.0 mmol) was added to 10 ml of 0.3 M solution of dichlorine heptoxide in carbon tetrachloride and the mixture was stirred for 48 hrs. The reaction mixture was quenched with ice and the organic layer was separated and dried over sodium sulfate. The yield (nmr) was 67%. Evaporation of solvent from an aliquot gave a colorless oil which was vacuum transferred at 0.03 mm to a -78° receiver: nmr (CCl_4) δ 5.32 (s, 2 H, $-\text{CH}_2\text{OCIO}_3$), and 2.32 ppm (s, 3 H, CH_3); ir (CCl_4) 3005 (w), 2950 (m), 2800 (w), 1590 (vs), 1425 (m), 1280 (vs), 1245 (vs), 1120 (m), 1040 (s), 1010 (s), 980 (s), and 840 cm^{-1} (m); d (25°), 1.601.

Anal. Calcd for $\text{C}_3\text{H}_5\text{ClN}_2\text{O}_8$: C, 15.48; H, 2.18; Cl, 15.25; N, 12.05. Found: C, 16.40; H, 1.92; Cl, 15.36; N, 11.68.

2-Fluoro-2,2-dinitroethyl Perchlorate. 2-Fluoro-2,2-dinitroethanol (0.51 g, 3.25 mmol) was added to 15 ml of a 0.3 M solution of dichlorine heptoxide in carbon tetrachloride at room temperature, and the mixture was stirred for 96 hrs. The reaction mixture was quenched with ice and the organic layer was separated and dried over sodium sulfate. The

yield was 60%. Evaporation of solvent (60 mm) from an aliquot left a colorless oil which was vacuum transferred at 0.05 mm to a -78° receiver: nmr (CCl_4) δ 5.56 ppm (d, $J_{\text{HF}}=15$ Hz); ir (CCl_4), 3005 (w), 2950 (m), 2800 (w), 1590 (vs), 1425 (m), 1280 (vs), 1245 (vs), 1120 (m), 1040 (s), 1010 (s), 980 (s), and 840 cm^{-1} (m); $d(25^{\circ}) = 1.704$.

Anal. Calcd for $\text{C}_2\text{H}_2\text{ClFN}_2\text{O}_3$: C, 10.16; H, 0.85; F, 8.03. Found: C, 10.17; H, 0.52; F, 8.51.

2-(2-Fluoro-2,2-dinitroethoxy) ethyl Perchlorate. 2-(2-Fluoro-2,2-dinitroethoxy)ethanol (0.118 g, 0.6 mmol) was added to 2 ml of 0.3 M dichlorine heptoxide in carbon tetrachloride at room temperature, and the mixture was stirred for 18 hrs. The carbon tetrachloride layer was washed with water and was dried over magnesium sulfate. Nmr analysis indicated a 43% yield: nmr (CCl_4), δ 4.57 (A_2B_2 multiplet, 2 H, CH_2OCIO_3), 4.58 (d, 2 H, $J_{\text{HF}} = 17$ Hz, $\text{FC} - \text{CH}_2 - \text{O}$), and 4.00 ppm (A_2B_2 , 2 H, $\text{OCH}_2 - \text{CH}_2\text{OCIO}_3$); ir (CCl_4) 2950 (m), 1600 (vs), 1460 (m), 1355 (w), 1320 (s), 1285 (vs), 1245 (vs), 1160 (s), 1050 (s), 1015 (s), 885 (m), 855 (m), and 710 cm^{-1} (s).

Allyl Perchlorate. Allyl alcohol (0.035 g, 0.6 mmol) was added to 2.5 ml of 0.3 M dichlorine heptoxide in carbon tetrachloride and 0.2 g of sodium sulfate at 0° with stirring. After 30 min. the solution was washed with ice water and dried over sodium sulfate. Allyl perchlorate was obtained in 48% yield: nmr (CCl_4) δ 5.73 (ABC multiplet, 3 H, $\text{CH}_2 = \text{CH}$), and 4.93 ppm (m, 2 H, CH_2OCIO_3); ir (CCl_4) 1640 (w), 1430 (w), 1280 (vs), 1240 (vs), 1050 (s), 1000 (w), 950 (s), 940 (m), 900 (m), and 720 cm^{-1} (s).

Allyl perchlorate was also prepared independently from silver perchlorate

and allyl bromide in carbon tetrachloride and had spectral properties identical with the material prepared above.

Propargyl Perchlorate. A mixture of 0.084 g (1.5 mmol) of propargyl alcohol, 5 ml of 0.3 M dichlorine heptoxide in carbon tetrachloride, and 0.5 g of sodium sulfate was stirred for 30 min. at 0°. The carbon tetrachloride layer was washed with ice water and dried over magnesium sulfate. The yield of propargyl perchlorate was 43%: nmr (CCl_4) δ 5.10 (d, 2 H, $J = 2$ Hz, $\text{C}\equiv\text{C}-\text{CH}_2\text{OCIO}_3$) and 2.72 ppm (t, 1 H, $J = 2$ Hz, $\text{HC}=\text{C}-$); ir (CCl_4) 3325 (m), 2960 (w), 2260 (w), 1460 (m), 1350 (w), 1330 (w), 1280 (vs), 1250 (vs), 1040 (s), 980 (m), 940 (s), 905 (s), and 690 cm^{-1} (s).

Isopropyl Perchlorate. This compound was obtained in 48% yield by the general procedure. Nmr (CCl_4) δ 5.10 (septet, 1 H, $J = 6$ Hz, $\text{CH}-\text{OCIO}_3$), and 1.58 ppm (d, 6 H, $J = 6$ Hz, CH_3); ir (CCl_4), 2990 (m), 1470 (m), 1395 (m), 1385 (m), 1275 (vs), 1240 (vs), 1115 (m), 1035 (s), 900 (s), and 720 cm^{-1} (s).

2-Hexyl Perchlorate. 2-Hexanol (0.061 g, 0.6 mmol) was added to 2 ml of 0.3 M dichlorine heptoxide in carbon tetrachloride and the solution was stirred for 3 hrs at ambient temperature. The solution became greenish-yellow and some oil separated. The reaction mixture was stirred with water and the carbon tetrachloride layer was separated and dried. Nmr analysis showed a 62% yield of 2-hexyl perchlorate and an 8% yield of 2-hexanone. The identity of 2-hexanone was established by spectral and glpc comparison with an authentic sample. 3-Hexyl perchlorate was not observed within the limits of detection by nmr, estimated to be about 10% because of overlap. The spectral properties of 2-hexyl perchlorate are: nmr (CCl_4) δ 4.85 (m, 1 H, CHOCIO_3), 1.57 (broad m, 6 H, $-\text{CH}_2-$), 1.48 (d, 3 H, $J = 6$ Hz,

$\text{CH}_3\text{-CH}(\text{OCLO}_3)$, and 0.93 ppm (m, 3 H, CH_3 -); ir (CCl_4) (mixture), 2980 (s), 2910 (m), 1715 (m), 1470 (m), 1395 (m), 1310 (m), 1275 (vs), 1240 (vs), 1190 (w), 1050 (s), 910 (w), and 720 cm^{-1} (s).

3-Hexyl Perchlorate. By the above procedure, 3-hexanol gave a 53% yield of 3-hexyl perchlorate, a 9% yield of 3-hexanone, and a 6% yield of 3-hexyl perchlorate (doublet at 1.48). The spectra for 3-hexyl perchlorate are as follows: nmr (CCl_4) δ 4.85 (m, 1 H, CHOCLO_3), 1.57 (broad m, 6 H, CH_2), and 1.03 ppm (m, 6 H, CH_3); ir (CCl_4) (mixture) 2980 (s), 2920 (m), 1710 (m), 1470 (m), 1400 (w), 1280 (vs), 1250 (vs), 1050 (s), 910 (m), 880 (m), and 730 cm^{-1} (s).

Perfluoro-t-butyl Perchlorate. Perfluoro-t-butanol (0.354 g, 1.5 mmol) was added to 0.30 ml of 5 N sodium hydroxide and the salt was dried for 5 hrs at 0.1 mm Hg. The residue was stirred for 18 hrs with 5 ml of 0.3 M dichlorine heptoxide in carbon tetrachloride. Fluorine nmr analysis of the solution, using hexafluorobenzene as a quantitative internal standard, showed a 33% yield of perfluoro-t-butyl perchlorate, ϕ 68.20, and a 56% yield of perfluoro-t-butanol, ϕ 74.61. The perfluoro-t-butanol was removed by washing the carbon tetrachloride solution with 1 N sodium hydroxide solution. Ir (CCl_4): 1295 (vs), 1275 (vs), 1230 (m), 1095 (s), 1040 (s) and 995 cm^{-1} (s). The glpc retention time of the material was too close to that of carbon tetrachloride to allow facile preparative isolation.

1,1,1,3,3,3-Hexafluoro-2-phenyl-2-propyl Perchlorate. Sodium hydride (0.115 g, 4.6 mmol) was added to a solution of 0.7355 g (3.01 mmol) of 1,1,1,3,3,3-hexafluoro-2-phenyl-2-propanol, and the mixture was heated briefly to 50° . The mixture was cooled to 0° and 10 ml of 0.3 M dichlorine heptoxide in carbon tetrachloride was added. The reaction mixture was

stirred for 1 hr at ambient temperature, and then for 30 min after 1 ml of water was added. The carbon tetrachloride layer was dried over sodium sulfate. Fluorine nmr using hexafluorobenzene as a quantitative internal standard, showed a 50% yield of 1,1,1,3,3,3-hexafluoro-2-phenyl-2-propyl perchlorate, δ 69.33, and a 29% yield of 1,1,1,3,3,3-hexafluoro-2-phenyl-2-propanol, δ 76.04. The alcohol was removed by extracting the carbon tetrachloride solution with 1 N sodium hydroxide. An analytical sample of the perchlorate was obtained by preparative glpc (20 min retention time, 80°, 60 ml He/min): proton nmr, δ 7.68 (sym m); ir (CCl₄), 1290 (vs), 1235 (vs), 1200 (s), 1170 (m), 1000 (m) and 980 (m) cm⁻¹. Elemental analyses for hydrogen and fluorine were obtained by nmr integration of a weighed sample using 1,2-dichloroethane and hexafluorobenzene, respectively, as standards.

Anal. Calcd for C₉H₅F₆ClO₄: H, 1.41; F, 34.90 Found: H, 1.41; F, 34.43.

1,1,1,3,3,3-Hexafluoro-2-methyl-2-propyl Perchlorate. Sodium hydride (0.0251 g, 1.05 mmol) was added to 0.1707 (0.938 mmol) of 1,1,1,3,3,3-hexafluoro-2-methyl-2-propanol and the mixture was heated to 50°. Dichlorine heptoxide in carbon tetrachloride (3.5 ml, 1.05 mmol) was added at 0° and the mixture was stirred 18 hrs at ambient temperature. The solution was stirred 30 min with 1 ml of water and was dried over sodium sulfate. Nmr analysis showed a 15 % yield of 1,1,1,3,3,3-hexafluoro-2-methyl-2-propyl perchlorate and an 83% yield of the alcohol. The latter was removed by washing with 1 N sodium hydroxide: proton nmr (CCl₄), δ 2.17 ppm (broad s); fluorine nmr, δ 76.86 ppm (s); ir (CCl₄), 1290 (vs), 1260 (s), 1230 (vs), 1190 (m), 1140 (m), 1120 (m), 1090 (s) and 1030 (s) cm⁻¹.

Reaction of Perchlorates with Lithium Bromide. A solution of 2.0 mmol of 1,4-butanediperchlorate in 8 ml of carbon tetrachloride was added dropwise with stirring at 0° to 8 ml of 10% lithium bromide in acetone. The solution was stirred at ambient temperature for 45 min, washed with water, dried and stripped of solvent to give 0.404 g (94%) of 1,4-dibromobutane, identified by spectral and glpc comparison with an authentic sample. The same procedure using pentyl perchlorate, 1,2-ethanediperchlorate, and propargyl perchlorate gave 90-100% yields of the corresponding bromides.

Reaction of Pentyl Perchlorate with Pentanol. Pentanol (0.053 g, 0.6 mmol) and potassium carbonate (0.276 g, 2 mmol) were added to a solution of 0.6 mmol of pentyl perchlorate in 3 ml of carbon tetrachloride and the mixture was stirred at ambient temperature. Dipentyl ether was formed in 5% yield in 20 hrs, 25% in 4 days and 90% in 8 days. The reaction was monitored by nmr, and the product was identified by glpc comparison with an authentic sample.

Reaction of Isopropyl Perchlorate with Pentanol. Pentanol (0.026 g, 0.3 mmol) and sodium sulfate (0.142 g, 1 mmol) were added to a solution of 0.3 mmol of isopropyl perchlorate in 2 ml of carbon tetrachloride and the mixture was stirred. Isopropyl pentyl ether was formed in 25% yield in 18 hrs. 50% in 3 days and 85% in 6 days.

Reaction of Allyl Perchlorate with 2-Fluoro-2,2-dinitroethanol. To a solution of 0.72 mmol of allyl perchlorate in 5 ml of carbon tetrachloride was added 5 ml of methylene chloride, 0.30 g (2 mmol) of 2-fluoro-2,2-dinitroethanol²⁴ and 0.69 g (5 mmol) of potassium carbonate. The mixture was stirred for 48 hrs. The solution was washed with water and with 5% sodium hydroxide, dried over sodium sulfate, and the solvent was removed to give

0.11 g (79%) of allyl 2-fluoro-2,2-dinitroethyl ether, identical with an authentic sample²⁵.

Reaction of Hexyl Perchlorate with Dimethyl Sulfoxide. Dimethyl sulfoxide (5 ml) and 0.5 g (6 mmol) of sodium bicarbonate were added to a solution of 1.74 mmol of hexyl perchlorate in 10 ml of carbon tetrachloride. An initially exothermic reaction took place, and nmr spectra showed the immediate consumption of perchlorate and slow formation of hexaldehyde. After 24 hrs the mixture was washed with water and dried. The only products detected by nmr were hexaldehyde (95% yield) and dimethyl sulfide. Vacuum distillation gave pure hexaldehyde.

References

1. This work was supported by the Office of Naval Research.
2. A. Michael and W. T. Conn, J. Amer. Chem. Soc., 23, 445 (1900).
3. F. Meyer and H. G. Kessler, Chem. Ber., 54B, 566 (1921).
4. C. F. Goodeve and J. Powney, J. Chem. Soc., 2078 (1932).
5. A. A. Zinov'ev and V. Ya. Rosolovskii, Zhur. Neorg. Khim., 1, 2596 (1956).
6. V. Ya. Rosolovskii, A. A. Zinov'ev and V. A. Prokhorov, Zhur. Neorg. Khim., 5, 2148 (1960).
7. A. Pavia, Compt. Rend., 261, 5118 (1965).
8. E. Colocchia, R. V. Figini and H. J. Schumacher, Angew. Chem., 68, 492 (1956).
9. R. Fonteyne, Naturw. Tijdschr. 20, 112 (1938).
10. R. Savoie and P. A. Giguere, Can. J. Chem., 40, 991 (1962).
11. Z. Spurny, Talanta, 9, 885 (1962).
12. R. J. Gillespie and E. A. Robinson, Can. J. Chem., 42, 2496 (1964).
13. J. Meyer and W. Spormann, Z. Anorg. Chem., 228, 341 (1936).
14. G. Radell, J. W. Connolly and A. J. Raymond, J. Amer. Chem. Soc., 83, 704 (1960),
reported the synthesis of several primary alkyl perchlorates from alkyl
iodides and silver perchlorate, but the detection of isomerization would
have been unlikely since nmr was not available. Our repetition of their
procedures yielded mixtures containing mainly secondary isomers. This
work will be reported elsewhere.
15. D. M. Hoffman, J. Org. Chem., 36, 1716 (1971), reported the preparation
of mixtures of secondary perchlorates by the reaction of perchloric acid
and sulfuric acid with olefins.
16. G. S. Hammond, M. F. Hawthorne, H. Waters and B. M. Graybill, J. Amer.
Chem. Soc., 82, 704 (1960).

17. S. Winstein and A. H. Fainberg, J. Amer. Chem. Soc., 80, 459 (1958).
18. H. Burton and D. A. Munday, J. Chem. Soc., 1456 (1954).
19. R. Stewart, Oxidation Mechanisms, Benjamin, New York 1964.
20. K. B. Wiberg (ed.), Oxidation in Organic Chemistry, Part A, Academic Press, New York, 1965.
21. K. M. Harmon, H. J. Dauben and L. R. Honnen, J. Org. Chem., 25, 1442 (1960).
22. C. J. Schack, D. Pilipovich and J. F. Hon, Inorg. Chem., 12, 897 (1973).
23. H. Snyder, P. L. Gendler and H. Chang, Synthesis, 655 (1971).
24. V. Grakauskas and K. Baum, J. Org. Chem., 33, 3080 (1968).
25. V. Grakauskas, J. Org. Chem., 35, 3030 (1970).

Reactions of Dichlorine Heptoxide with Amines¹

Charles D. Beard and Kurt Baum *

Contribution from Fluorochem, Inc., Azusa, California 91702

Abstract: Dichlorine Heptoxide in carbon tetrachloride reacts as a perchlorylating agent with secondary and primary amines. Piperidine, diethylamine, dipentylamine and 2-ethylaziridine gave N-perchlorylpiperidine, N-perchloryldiethylamine, N-perchloryldipentylamine and N-perchloryl-2-ethylaziridine, respectively. Hexylamine, butylamine, propylamine, iso-propylamine and t-butylamine gave N-perchlorylhexylamine, N-perchlorylbutylamine, N-perchlorylpropylamine, N-perchlorylisopropylamine and N-perchloryl-t-butylamine, respectively. The primary perchlorylamines are acidic and form sodium salts with aqueous sodium hydroxide; the ionization constant of N-perchloryl-t-butylamine is 1.5×10^{-7} . The salts of N-perchlorylhexylamine and N-perchlorylbutylamine were chlorinated with sodium hypochlorite. In carbon tetrachloride solution, primary alkyl N-perchlorylamines and the N-chloro derivatives give the corresponding carboxylic acids at ambient temperature, whereas N-perchlorylisopropylamine gives acetone and N-perchloryl-t-butylamine is unchanged.

Only two compounds with nitrogen-bonded perchloryl groups have been reported, the ammonium salt of perchlorylamide² and N-perchlorylpiperidine,³ which were prepared by reactions of perchloryl fluoride with ammonia and with piperidine. Attempts to extend this reaction to other amines gave only oxidation and fluorination products,⁴ and perchloryl fluoride was recently used as the reagent of choice for the fluorination of an amine.⁵ The function of dichlorine heptoxide in carbon tetrachloride solution as an effective and convenient perchlorylating agent for alcohols⁶ suggested that its reaction with amines might provide a practical route to perchlorylamines.

Dichlorine heptoxide in carbon tetrachloride reacted with secondary amines to give high yields of perchlorylamines, as shown in Table I. Two moles of amine were used per mole of dichlorine heptoxide, with one functioning as a base, and the reactions were complete on mixing the reagents. The perchlorylamines were obtained as carbon tetrachloride solutions, with no impurities detectable by nmr. Thus piperidine, diethylamine and dipentylamine gave N-perchlorylpiperidine, N-perchloryldiethylamine and N-perchloryldipentylamine, respectively. This reaction was even applicable to the preparation of a strained molecule such as N-perchloryl-2-ethylaziridine.

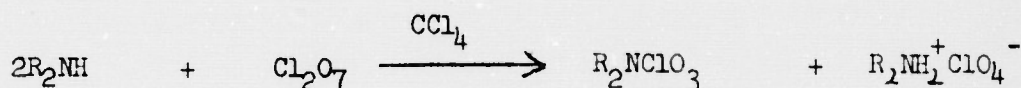
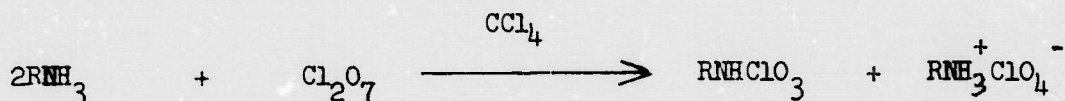


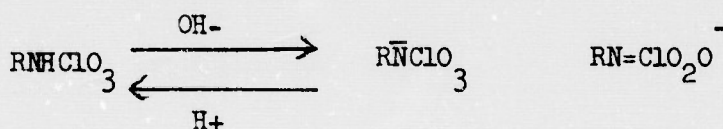
Table I Perchlorylamines from Amines and Dichlorine Heptoxide

<u>Starting Material</u>	<u>Product</u>	<u>Yield(%)</u>
		73
$(C_2H_5)_2NH$	$(C_2H_5)_2NClO_3$	77
$(C_5H_{11})_2NH$	$(C_5H_{11})NClO_3$	81
		83
$CH_3(CH_2)_4CH_2NH_2$	$CH_3(CH_2)_4CH_2NClO_3$	63
$CH_3(CH_2)_2CH_2NH_2$	$CH_3(CH_2)_2CH_2NClO_3$	61
$CH_3CH_2CH_2NH_2$	$CH_3CH_2CH_2NClO_3$	61
$(CH_3)_2CHNH_2$	$(CH_3)_2CHNHClO_3$	60
$(CH_3)_3CNH_2$	$(CH_3)_3CNHClO_3$	71

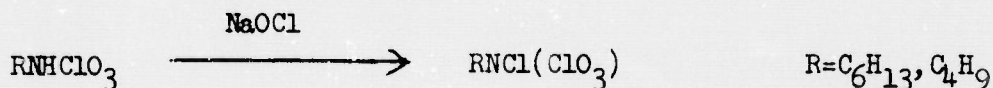
Primary amines reacted similarly to give the corresponding perchlorylamines. Thus, hexylamine, butylamine, and propylamine, as well as isopropylamine and even t-butylamine gave the corresponding perchlorylamines in yields of 60-71%.



The primary perchlorylamines comprise a new reactive organic functional group in that the hydrogens on nitrogen are acidic. The NH was exchanged with D₂O on mixing. The compounds were extracted from carbon tetrachloride by aqueous sodium hydroxide and recovered quantitatively on acidification. The ionization constant of N-perchloryl-t-butylamine, determined by potentiometric titration, was 1.51×10^{-7} . The first ionization constant of the parent perchlorylamide, H₂NClO₃, was reported² to be 3.0×10^{-6} .



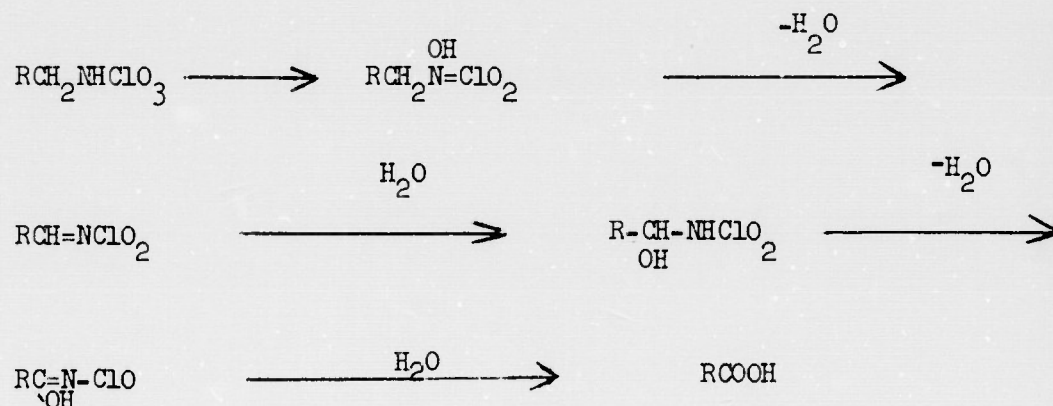
N-perchlorylhexylamine and N-perchlorylbutylamine in carbon tetrachloride solution were chlorinated by stirring with aqueous sodium hypochlorite. The ir and nmr spectra of the products were consistent with the corresponding N-chloro-N-perchlorylamine structures and showed no evidence of NH bonds. The products were not extractable with 1 N sodium hydroxide. Yields were 84-87%. N-perchloryl-t-butylamine was not chlorinated under these conditions, probably because of steric hinderance.



Primary perchlorylamines with α -hydrogens were found to undergo a self-oxidation reaction at ambient temperature in carbon tetrachloride solution. Thus, N-perchlorylpropylamine was completely converted to propionic acid in 18 hrs, and N-perchlorylhexylamine to hexanoic acid in 3 days. Acetone was also formed from N-perchlorylisopropylamine under the same conditions.

Hexanoic acid was obtained similarly from N-chloro-N-perchlorylhexylamine. On the other hand, N-perchloryl-t-butylamine gave no detectable decomposition in a week under the same conditions, and the N-perchloryl derivatives of secondary amines also gave no evidence of decomposition.

The formation of carboxylic acids from primary alkyl perchlorylamines can be rationalized on the basis of a mechanism such as the following:



The acidic perchlorylamines are assumed to be in tautomeric equilibrium with their enolic isomers. The α -hydrogens of the latter could be sufficiently labile for isomerization to the corresponding hydroxychlorylamines by elimination and readdition of water, and repetition of this process would yield carboxylic acids. A similar route can be envisioned for the formation of ketones from secondary alkyl derivatives. Acids could be formed similarly from N-chloroperchlorylamines by the initial elimination of HCl or by preliminary

hydrolysis to HOCl and the N-perchlorylamine. This reaction path has similarities to that of the conversion of nitroalkanes to carboxylic acids, in which hydroxamic acids are intermediates.⁷



Other possible mechanisms for these reactions involve an initial α -elimination or β -elimination of HClO_3 , which subsequently acts as an oxidizing agent. The stability of N-perchloryl-t-butylamine, however, argues against an α -elimination route, while the stability of perchloryl derivatives of secondary amines argues against β -elimination routes.

The spontaneous formation of carboxylic acids from primary N-perchlorylamines offers an attractive synthetic method for the direct conversion of primary amines to acids. The addition of an amine to the dichlorine heptoxide-carbon tetrachloride reagent gives a carbon tetrachloride solution of the perchlorylamine on mixing, which on standing at room temperature, gives the carboxylic acid in high overall yields.

Experimental Section

Nmr spectra were recorded with a Varian T-60 spectrometer, and ir spectra were recorded with a Perkin-Elmer 700 spectrometer. Perchlorylamines should be used in solution where possible. The neat materials are sensitive explosives and should be handled only with adequate protective devices.

N-Perchlorylpiperidine. Piperidine (0.104 g, 1.2 mmol) was added dropwise with stirring to 2 ml of 0.3 M dichlorine heptoxide in carbon tetrachloride⁶ at 0°. After 5 min, the mixture was washed with dilute sulfuric acid and then with water. The carbon tetrachloride solution was dried over molecular sieves. Analysis of the solution by nmr using chlorobenzene as a quantitative internal standard showed a 73% yield of N-perchlorylpiperidine: nmr (CCl₄) δ 3.42 (t, J=6 Hz, 4 H, N-CH₂) and 1.85 ppm (broad m, 6 H). The ir spectrum was identical with that reported².

N-Perchloryldiethylamine. The reaction of 0.22 g (3.0 mmol) of diethylamine with 5 ml of 0.3 M dichlorine heptoxide in carbon tetrachloride by the above procedure gave a 77% yield of N-perchloryldiethylamine: nmr (CCl₄) δ 3.47 (broadened q, 4 H, CH₂) and 1.37 ppm (t, 6 H, J = 6 Hz, CH₃); ir (CCl₄) 1240 (vs), 1200 (vs), 1010 (s), and 680 cm⁻¹ (s).

N-Perchloryldipentylamine. By the above procedure, N-perchloryldipentylamine was obtained in 81% yield: nmr (CCl₄) δ 3.27 (m, 4 H, CH₂NClo₃), 1.47 (broad m, 12 H, -CH₂-) and 0.93 ppm (distorted t, 6 H, CH₃); ir (CCl₄) 1240 (s), 1200 (s), 1020 (s) and 680 cm⁻¹ (m).

N-Perchloryl-2-ethylaziridine. The above procedure gave an 83% yield of N-perchloryl-2-ethylaziridine. An analytical sample was obtained by removing solvent under vacuum and vacuum transferring the residue to a -78° receiver at 0.05 mm: nmr (CCl₄) δ 2.85 (broad m, 3 H, $\overset{\text{N}}{\text{CH}}\text{-CH}_2$), 1.67 (m, 2 H, $\overset{\text{N}}{\text{CH}_2}$)

and 1.30 ppm (distorted t, 3 H, CH_3); ir (CCl_4) 1245 (vs), 1210 (vs), 1020 (vs) and 680 cm^{-1} (s)

Anal. Calcd for $\text{C}_4\text{H}_8\text{NClO}_3$: C, 31.28; H, 5.25; Cl, 24.08. Found: C, 30.76; H, 4.81; Cl, 23.57.

N-Perchlorylbutylamine. The reaction of butylamine with dichlorine heptoxide, as above, gave a 61% yield of N-perchlorylbutylamine: nmr (CCl_4) δ 5.77 (broad s, 1 H, NH, disappeared on addition of D_2O), 3.40 (t, 2 H, CH_2N), 1.53 (m, 4 H, CH_2CH_2) and 0.97 ppm (m, 3 H, CH_3); ir (CCl_4) 3280 (m, NH), 1245 (s), 1215 (vs), 1030 (s) and 670 cm^{-1} (s).

N-Perchloryl-t-butylamine. The above procedure gave a 71% yield of N-perchloryl-t-butylamine: nmr (CCl_4) δ 7.10 (broad s, 1 H, NHClO_3 , disappeared on addition of D_2O) and 1.32 ppm (s, 9 H, CH_3); ir (CCl_4) 3280 (m, NH), 1260 (s), 1210 (vs), 1020 (vs) and 660 cm^{-1} (s). The carbon tetrachloride solution underwent no visible or spectral changes within one week at ambient temperature.

An analytical sample was obtained by vacuum transfer to a -78° receiver at 0.02 mm.

Anal. Calcd for $\text{C}_4\text{H}_{10}\text{NClO}_3$: C, 30.86; H, 6.46; Cl, 22.87. Found: C, 29.62; H, 6.47; Cl, 22.62.

Potentiometric titration gave an equivalent weight of 151.4 (calcd 155) and an ionization constant of 1.51×10^{-7}

N-Perchlorylhexylamine. The above procedure gave a 63% yield of N-perchlorylhexylamine: nmr (CCl_4) δ 6.73 (broad t, 1 H, NHClO_3 , disappeared on addition of D_2O), 3.42 (q, 2 H, CH_2N), 1.40 (m, 8 H, CH_2CH_2) and 0.93 ppm (distorted t, 3 H, CH_3); ir (CCl_4) 3290 (w, OH), 1240 (sh), 1210 (vs), 1020 (s) and 665 cm^{-1} (s). On standing at ambient temperature for 3 days, the compound was completely converted to hexanoic acid and an unidentified salt-like solid. Hexanoic acid was identified by ir, nmr and glpc comparison with an authentic sample.

N-Perchlorylpropylamine. The above procedure gave N-perchlorylpropylamine in 61% yield: nmr (CCl_4) δ 6.9 (broad, 1 H, NHClO_3), 3.4 (m, 2 H, CH_2N), 1.72 (m, 2 H, CH_2CH_3) and 1.07 ppm (t, $J=6$ Hz, CH_3); ir (CCl_4) 3270 (m, NH), 1250 (s), 1240 (sh), 1210 (vs), 1030 (vs) and 645 cm^{-1} (s). The compound was completely converted in 18 hrs at ambient temperature to propionic acid and an unidentified salt-like material.

N-Perchlorylisopropylamine. The above procedure gave N-perchlorylisopropylamine in 60% yield: nmr (CCl_4) δ 6.7 (broad, 1 H, NHClO_3), 3.83 (m, 1 H, CH) and 1.33 ppm (d, $J=7$ Hz, CH_3); ir (CCl_4) 3270 (m, NH), 1230 (sh), 1205 (vs), 1020 (vs) and 660 cm^{-1} (s). The compound in carbon tetrachloride was 60% converted to acetone in one week.

Sodium Salts of N-Perchloryl Primary Amines. Extracting the carbon tetrachloride solutions of N-perchloryl primary amines with 1 N sodium hydroxide left nothing in the carbon tetrachloride layer observable by nmr. Acidification of the aqueous layer resulted in reextraction of the starting material with no change in nmr and in ir spectra.

N-Chloro-N-perchloryl-hexylamine. A solution of 0.95 mmol of N-perchlorylhexylamine in 5 ml of carbon tetrachloride was stirred for 5 min. with 5 ml of 5% aqueous sodium hypochlorite, and the organic layer was dried. Nmr and ir spectra of the solution showed no evidence of NH, and the product was not affected by extraction with 1 N sodium hydroxide. Analysis by nmr using chlorobenzene as a quantitative reference indicated an 87% yield of N-chloro-N-perchloryl hexylamine: nmr (CCl_4) δ 3.70 (t, $J=6$ Hz, 2 H, CH_2N), 1.40 (broad m, 8 H, $-\text{CH}_2-$) and 0.90 ppm (distorted t, 3 H, CH_3); ir (CCl_4) 1250 (vs), 1220 (vs), 1020 (s), 975 (m), and 650 cm^{-1} (m). The compound in carbon tetrachloride was completely converted to hexanoic acid in 20 hrs.

N-Chloro-N-perchlorylbutylamine. By the above procedure, 0.92 mmol of N-perchlorylbutylamine in 5 ml of carbon tetrachloride gave an 84% yield of N-chloro-N-perchlorylbutylamine: nmr (CCl_4) δ 3.65 (t, $J=6$ Hz, 2 H, CH_2N), 1.7 (broad m, 4 H, CH_2) and 1.0 ppm (distorted t, 3 H, CH_3); ir (CCl_4) 1250 (vs), 1220 (vs), 1020 (vs) and 650 cm^{-1} (s).

References

1. This work was supported by the Office of Naval Research.
2. H. C. Mandell, Jr. and G. Barth-Wehrenalp, J. Inorg. Nucl. Chem., 12, 90 (1959).
3. D. M. Gardner, R. Helitzer and C. J. Mackley, J. Org. Chem., 29, 3738 (1964).
4. D. M. Gardner, R. Helitzer and D. H. Rosenblatt, J. Org. Chem., 32, 1115 (1967).
5. J. Cantacuzene and J. Leroy, J. Amer. Chem. Soc., 93, 5263 (1971).
6. J. Amer. Chem. Soc., preceding manuscript.
7. S. B. Lippincott and H. B. Hass, Ind. and Eng. Chem., 31, 118 (1939).

Appendix C

Reactions of Dichlorine Heptoxide and of

Acyl Perchlorates with Ethers

Kurt Baum and Charles D. Beard

Contribution from Fluorochem Inc., Azusa, California 91702

Abstract: Ether cleavages by dichlorine heptoxide and acyl perchlorates were studied. Acetyl perchlorate, benzoyl perchlorate and N,N-diethylcarbamoyl perchlorate were obtained in carbon tetrachloride solution from the acid chlorides and silver perchlorate. Their solubility and spectral properties indicated covalent structures rather than acylium salts. Acetyl perchlorate reacted with tetrahydrofuran to give 4-perchloratobutyl acetate and with epoxides to give vicinal acetoxyperchlorates. Isopropyl ether gave isopropyl perchlorate and isopropyl acetate whereas isopropyl pentyl ether gave isopropyl perchlorate and pentyl acetate. Dimethoxymethane gave methyl acetate and methoxymethyl perchlorate. Benzoyl perchlorate and N,N-diethylcarbamoyl perchlorate were reacted with tetrahydrofuran to give the corresponding 4-perchloratobutyl esters. Dichlorine heptoxide in carbon tetrachloride reacted with tetrahydrofuran and with trimethylene oxide to give 1,4-butanediperchlorate and 1,3-propanediperchlorate, respectively. 2,3-Butene oxide gave 2,3-butanediperchlorate in low yield. Ethyl ether gave ethyl perchlorate and a trace of ethyl acetate. Propyl ether gave propyl perchlorate and isopropyl perchlorate, whereas isopropyl ether gave isopropyl perchlorate and 2,2-diperchloratopropane. Dimethoxymethane and dichlorine heptoxide gave methyl perchlorate and methoxymethyl perchlorate.

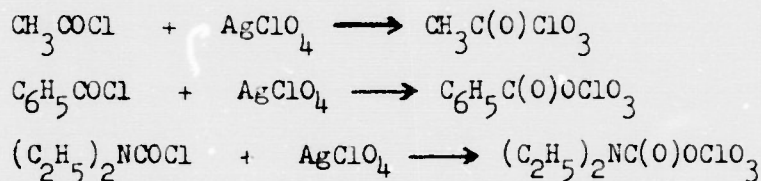
Dichlorine heptoxide in carbon tetrachloride was shown recently to be an effective perchlorylating agent for alcohols² and for amines³. The present paper deals with reactions of this little explored reagent and of related acyl perchlorates with ethers.

The use of acyl perchlorates in solvents such as ether, nitromethane, and acetic acid as acetylating agents has been reported⁴⁻⁶. In a review of this class of compounds⁷, Olah and Quinn questioned earlier assumptions that acyl perchlorates are ionic acylium salts, $[RC=O]^+ClO_4^-$, because their acylating power and stability are lower than those of known acylium salts. Solubilities in nonpolar solvents and spectral properties, which should readily differentiate between the ionic and covalent structures, have not been reported.

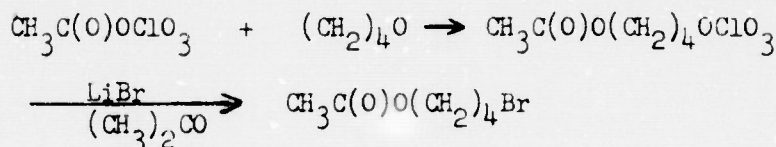
Acetyl chloride was found to react on mixing with a suspension of silver perchlorate in carbon tetrachloride to give a solution of acetyl perchlorate. The yield, determined by nmr, was essentially quantitative. The nmr chemical shift of the compound, δ 2.27, is close to those of acetyl halides and anhydrides, whereas values reported for CH_3CO^+ salts⁸ are approximately δ 4.0. The infrared spectrum of acetyl perchlorate shows a normal carbonyl peak at 1825 cm^{-1} rather than the peak at 2300 cm^{-1} assigned to CH_3CO^+ salts⁸. Solutions of acetyl perchlorate in methylene chloride, chloroform and ethylene chloride were also prepared by adding acetyl chloride to suspensions of silver perchlorate in these solvents. The solubility properties and spectra of acetyl perchlorate are thus clearly consistent with the covalent structure, $CH_3C(O)-OClO_3$.

Electron-supplying substituents would increase the likelihood for an acyl perchlorate to exist as an acylium salt. Benzoyl perchlorate and N,N-diethyl-carbamoyl perchlorate were therefore prepared from the corresponding acid chlorides and silver perchlorate in carbon tetrachloride. The compounds were soluble

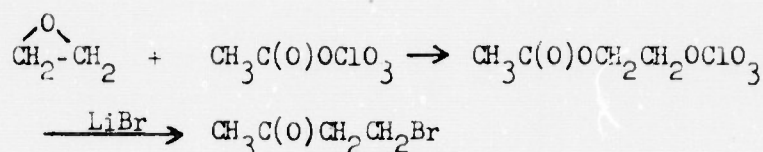
in carbon tetrachloride, and their spectral properties were similar to those of acetyl perchlorate. Thus even an adjacent phenyl or amino group to stabilize positive charge is not sufficient to impart salt-like properties to an acyl perchlorate.



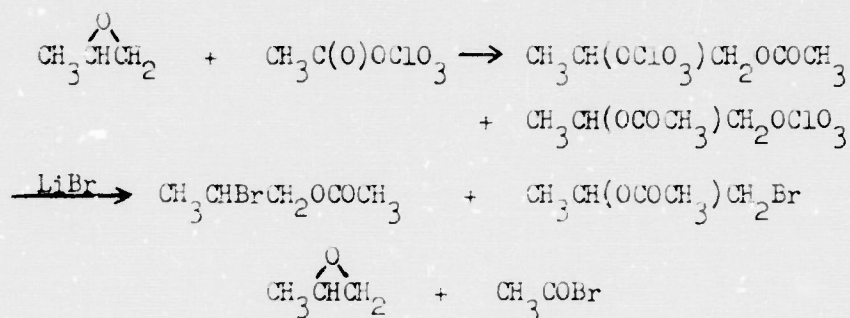
Acyl perchlorates in carbon tetrachloride reacted cleanly with cyclic ethers to give α,ω -acetoxyp perchlorates. Thus, acetyl perchlorate in carbon tetrachloride reacted rapidly with tetrahydrofuran at 0° to give a 78% yield of 4-perchloratobutyl acetate, identified by ir and nmr spectra and by conversion to 4-bromobutyl acetate with lithium bromide in acetone. No 1,4-butanediperchlorate or 1,4-diacetyoxybutane were formed, which would be expected if acetyl perchlorate equilibrates to dichlorine heptoxide and acetic anhydride.



Epoxides readily added acetyl perchlorate to give vicinal acetoxyp perchlorates. Thus, ethylene oxide gave an 89% yield of 2-perchloratoethyl acetate, identified spectrally and by conversion to 2-bromoethyl acetate.

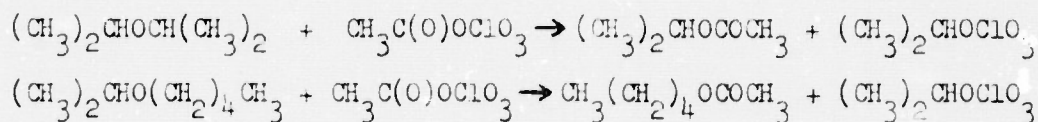


Propylene oxide gave an 80% yield of 2-perchlorato-1-propyl acetate and an 8% yield of 1-perchlorato-2-propyl acetate. Reaction of the mixture with lithium bromide in acetone gave the corresponding bromoacetates, which were prepared independently from acetyl bromide and propylene oxide.

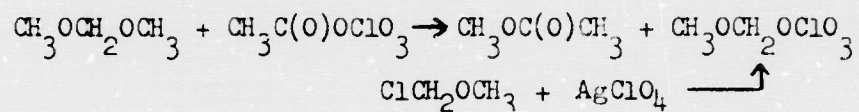


Epichlorohydrin similarly gave a mixture of 1-perchlorato-3-chloro-2-propyl acetate and 2-perchlorato-3-chloro-1-propyl acetate. 2-Butene oxide gave 3-perchlorato-2-butyl acetate.

Secondary alkyl ethers were also cleaved readily. Thus, isopropyl ether reacted with acetyl perchlorate in carbon tetrachloride to give essentially quantitative yields of isopropyl perchlorate and isopropyl acetate. Similarly, isopropyl pentyl ether gave isopropyl perchlorate and pentyl acetate, with no detectable trace of pentyl perchlorate or isopropyl acetate. Simple primary dialkyl ethers were less readily cleaved by acetyl perchlorate. Ethyl ether, propyl ether and pentyl ether gave ethyl acetate, propyl acetate and pentyl acetate, respectively, in yields of 20-25%, but no alkyl perchlorates were detected.

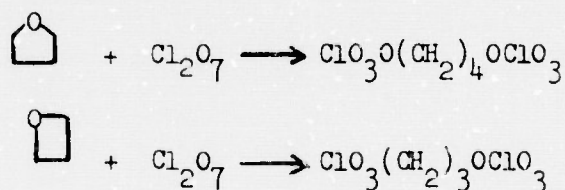


Acetals were also cleaved by acetyl perchlorate. Thus, dimethoxymethane gave methyl acetate and methoxymethyl perchlorate. The latter compound was also synthesized independently from silver perchlorate and chloromethyl methyl ether.



Benzoyl perchlorate and N,N-diethylcarbamoyl perchlorate also reacted with tetrahydrofuran to give 4-perchloratobutyl benzoate and 4-perchloratobutyl N,N-diethylcarbamate, respectively. Reaction of these products with lithium bromide gave the corresponding 4-bromobutyl esters. The acyl perchlorates also gave high yields of the corresponding methyl esters on addition of methanol.

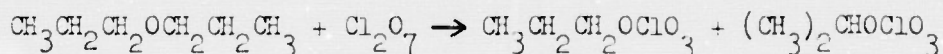
Reactions of ethers with dichlorine heptoxide were studied using the standard 0.3 M reagent in carbon tetrachloride described previously². Tetrahydrofuran was cleaved rapidly by this reagent to give an 83% yield of 1,4-butanediperchlorate. Trimethylene oxide gave 1,3-propanediperchlorate in 55% yield.



Epoxides also reacted with dichlorine heptoxide. An excess of dichlorine heptoxide and 2-butene oxide gave a 30% yield of 2,3-butanediperchlorate, but stoichiometric mixtures of the reagents gave a mixture of products, which appeared to contain oligomers. Regardless of the ratio of reactants, ethylene oxide, propylene oxide and epichlorohydrin gave complex mixtures which showed perchlorate bands in their ir spectra.

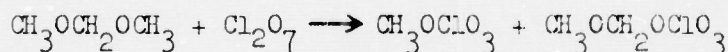
Simple aliphatic ethers were also cleaved with dichlorine heptoxide. The reaction of ethyl ether, monitored by nmr, was found to give a rapid initial reaction, yielding 33% ethyl perchlorate. The formation of ethyl perchlorate then became progressively slower; the yield was 53% in 2 hrs, 59% in 18 hrs, and 67% in 66 hrs. Apparently perchloric acid, formed in a side reaction, reduces the rate by complexing with unreacted ether. An acidic hydrogen appeared at δ 15.5-16.0, accompanied by a downfield shift of 0.28 ppm for the methylene hydrogens of ether. A 2-3% yield of ethyl acetate was also formed.

A similar effect was observed in the reaction of propyl ether with dichlorine heptoxide. In 15 hrs, a 49% yield of propyl perchlorate was obtained, as well as a 13% yield of isopropyl perchlorate.



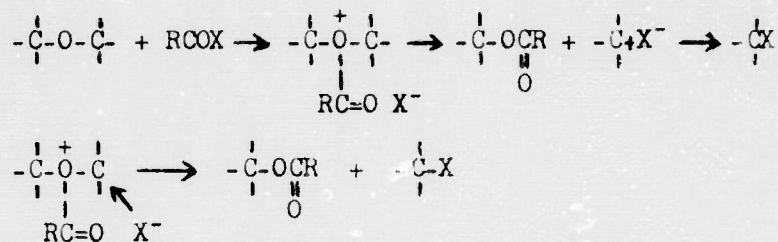
Isopropyl ether was also cleaved by dichlorine heptoxide in carbon tetrachloride to give a 10% yield of isopropyl perchlorate, but the major product was 2,2-diperchloratopropane, identified spectrally and by conversion to the 2,4-dinitrophenylhydrazone⁹. Isopropyl pentyl ether also gave this compound as well as low yields of isopropyl perchlorate and pentyl perchlorate.

Dimethoxymethane was cleaved by dichlorine heptoxide to give a 78% yield of methoxymethyl perchlorate and an 86% yield of methyl perchlorate in 5 days:

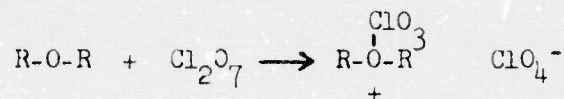


Ether cleavages by acylium ions and related species are generally assumed to take place through oxonium ion intermediates¹⁰⁻¹². Cleavage of the intermediates may take place by a spectrum of mechanisms ranging from $\text{S}_{\text{N}}1$ to $\text{S}_{\text{N}}2$, depending on the carbonium ion stability of the substrate fragment and the

strength of the nucleophile, as well as steric factors.



Lewis acid catalyzed cleavages of secondary and tertiary ethers by acid halides appear to go by an S_N1 type mechanism whereas primary ethers give S_N2 type products. Mechanisms of cleavages by mixed sulfonic carboxylic anhydrides are shifted toward the S_N1 end of the mechanistic spectrum because of the weak nucleophilic properties of sulfonate anions¹². This shift would be expected to be more pronounced for acyl perchlorates. A similar mechanism for cleavages by dichlorine heptoxide would involve a perchloryloxonium ion intermediate:



This strongly electron-withdrawing group on the oxonium ion should further enhance the tendency toward an S_N1 - like cleavage. The formation of a significant amount of isopropyl perchlorate from propyl ether and dichlorine heptoxide is thus noteworthy, since isopropyl derivatives were not found in the reaction of propyl ether with acetyl tosylate¹².

The formation of oxidation products from dichlorine heptoxide, particularly with isopropyl ethers, is also consistent with a perchloryloxonium ion intermediate, which has similarities to intermediates proposed for the oxidation of ethers by bromine¹³ and of alcohols by chromic acid¹⁴. Direct oxidation by dichlorine heptoxide can not be ruled out, however.

Experimental Section

Nmr spectra were recorded with a Varian T-60 spectrometer and ir spectra were recorded with a Perkin-Elmer 700 spectrometer. A Varian 920 gas chromatograph with a 5 ft x 0.25 in column of 12% QF-1 on chromosorb W was used for glpc separations.

Alkyl perchlorates are generally sensitive explosives, and the neat materials should be handled only with adequate protective devices.

Acetyl Perchlorate. Acetyl chloride (0.0785 g, 1 mmol) was added in two portions to a stirred suspension of 0.3 g (1.5 mmol) of silver perchlorate in 4 ml of carbon tetrachloride at 0°. The reaction mixture was stirred for 30 min and filtered to give a colorless solution which fumed in moist air. The yield was 96%, determined by nmr using ethylene chloride as internal standard. Solutions of acetyl perchlorate were stable for several days at room temperature. The same procedure was used to prepare acetyl perchlorate solutions in methylene chloride, chloroform and ethylene chloride. nmr (CCl_4) δ 2.27 ppm (s); ir (CCl_4) 1825 (vs), 1370 (w), 1285 (vs), 1160 (m), 1040 (s), 1095 cm^{-1} (m).

Reaction of Acetyl Perchlorate with Methanol. Excess methanol (1 ml) was added with stirring to 1 mmol of acetyl perchlorate in 4 ml carbon tetrachloride at 0°. The mixture was stirred for 30 min, washed with water, and dried. Nmr and ir spectra showed only methyl acetate obtained in 90% yield.

Reaction of Acetyl Perchlorate with Tetrahydrofuran. Tetrahydrofuran (0.072 g, 1 mmol) was added to 1 mmol of acetyl perchlorate in 4 ml carbon tetrachloride with stirring at 0°. The reaction mixture was stirred for 30 min, washed with water and dried. The only product in the carbon tetrachloride layer was 4-perchloratobutyl acetate in 78% yield (chlorobenzene as internal nmr standard): nmr (CCl_4) δ 4.52 (t, 2 H, $J = 6$ Hz, CH_2OCIO_3);

4.38 (t, 2 H, $J = 6$ Hz, CH_2OAc), 2.02 (s, 3 H, CH_3CO), and 1.88 ppm (m, 4 H, CH_2CH_2); ir (CCl_4) 1740 (C=O), 1280, 1240, 1040 cm^{-1} (OClO_3).

The solution of 4-perchloratobutyl acetate was added dropwise at room temperature to 5 ml of a 10% solution of lithium bromide in acetone. After 30 min, the reaction mixture was washed with water and dried. Evaporation of solvent gave 0.146 g (75%) of 4-bromobutyl acetate: nm4 (CCl_4) δ 4.02 (t, 2 H, $J = 6$ Hz, CH_2OAc), 3.37 (t, 2 H, $J = 6$ Hz, CH_2Br), 2.00 (s, 3 H, CH_3CO), and 1.87 ppm (m, 4 H, CH_2CH_2); ir (CCl_4) 1740, 1240 cm^{-1} (COO).

Anal. Calcd for $\text{C}_6\text{H}_{11}\text{BrO}_2$: C, 36.92; H, 5.64; Br, 40.99. Found: C, 36.69; H, 5.38; Br, 40.88.

Reaction of Acetyl Perchlorate with Isopropyl Ether. Isopropyl ether (0.102 g, 1 mmol) was added to a solution of 1 mmol of acetyl perchlorate in 4 ml carbon tetrachloride with stirring at 0° . Nmr spectra indicated completion of reaction in less than 10 min. The reaction mixture was washed with water and dried. Isopropyl perchlorate² and isopropyl acetate were obtained in 97% yield, identified by comparison with authentic samples by ir and nmr.

Reaction of Acetyl Perchlorate with Isopropyl Pentyl Ether. By the above procedure, acetyl perchlorate and isopropyl pentyl ether gave isopropyl perchlorate and n-pentyl acetate in 95 \pm 5% yield. Pentyl perchlorate and isopropyl acetate were not observed. Control experiments indicated that 1-2% of these components would have been detected.

Reaction of Acetyl Perchlorate with Primary Ethers. The appropriate primary ether (1 mmol) was added to 1 mmol of acetyl perchlorate in carbon tetrachloride with stirring at 0° . The solution immediately became yellow-orange and some insoluble material was formed. The only products observed either before or after treatment with water were the n-alkyl acetate (20-25% yield)

and starting material (45-50%). Thus, ethyl acetate, propyl acetate, and pentyl acetate were obtained from ethyl, propyl and pentyl ethers respectively. Increasing the reaction time to 48 hrs did not improve the yield and a dark tarry residue was deposited. In no case was any alkyl perchlorate detected.

Reaction of Acetyl Perchlorate with Ethylene Oxide. Ethylene oxide (0.088 g, 2 mmol) was added at 0° with stirring to a solution of 2 mmol of acetyl perchlorate in 10 ml of CCl_4 . The reaction mixture was stirred for 30 min, washed with water and dried. The nmr spectrum of the solution showed an 89% yield of 2-perchloratoethyl acetate ($\text{C}_6\text{H}_5\text{Cl}$ as quantitative standard): nmr (CCl_4) δ 4.60 (m, 2 H, A_2B_2 , CH_2OCIO_3), 4.27 (m, 2 H, A_2B_2 , CH_2OAc), and 2.10 ppm (s, 3 H, CH_3COO); ir (CCl_4) 1750 (COO), 1285, 1240, 1040 cm^{-1} (OCIO_3). Treatment of the CCl_4 solution with an excess of 10% lithium bromide in acetone gave 2-bromoethyl acetate (81%): nmr (CCl_4) δ 4.22 (t, 2 H, $J = 6.5$ Hz, CH_2OAc), 3.37 (t, 2 H, $J = 6.5$ Hz, CH_2Br), and 2.00 ppm (s, 3 H, CH_3COO). The infrared spectrum was identical with that of an authentic sample.

Reaction of Acetyl Perchlorate with Propylene Oxide. Propylene oxide (0.058 g, 1 mmol) was added to a solution of 1 mmol of acetyl perchlorate at 0° with stirring. After 30 min reaction mixture was washed with water and dried. Nmr spectra showed two compounds identified as 2-perchlorato-1-propyl acetate (80% yield) and 1-perchlorato-2-propyl acetate (8% yield): nmr (CCl_4) of 2-perchlorato-1-propyl acetate, δ 5.17 (m, 1 H, CHOCIO_3), 4.13 (m, 2 H, CH_2OAc), 2.07 (s, 3 H, OCOCH_3), and 1.52 ppm (d, 3 H, $J = 7$ Hz, $\text{CH}_3\text{-CH}$); nmr of 1-perchlorato-2-propyl acetate δ 5.10 (m, CHOAc), 4.48 (m, CH_2OCIO_3), 2.07 (s, CH_3COO), and 1.33 ppm (d, $J = 6$ Hz, $\text{CH}_3\text{-CH}$). The ir spectrum of the mixture had a strong carbonyl band at 1755 cm^{-1} and perchlorate

bands at 1280, 1240 and 1040 cm^{-1} .

The mixture of isomers in carbon tetrachloride was added dropwise to 5 ml of 10% bromide in acetone at room temperature. A mixture of 2-bromopropyl acetate (95%) and 1-bromo-2-propyl acetate (5%) was obtained. The structures were assigned by comparison of nmr and ir spectra with those of an independently prepared mixture described below.

Reaction of Acetyl Bromide with Propylene Oxide. Propylene oxide (2.90 g, 0.05 mol) dissolved in 10 ml of carbon tetrachloride was added dropwise (1 hr) to a solution of 6.15 g (0.05 mol) of acetyl bromide in 50 ml of carbon tetrachloride with a catalytic quantity of zinc bromide. The reaction mixture was then stirred for 1 hr, washed with water and dried. Evaporation of the solvent and distillation of the residual oil gave 6.55 g (72%) of a mixture of bromoacetates, bp $54-58^{\circ}$ (10 mm). The ratio of 1-bromo-2-propyl acetate to 2-bromo-1-propyl acetate was 2:1. Nmr (CCl_4) of 1-bromo-2-propyl acetate δ 4.87 (septet, 1 H, CHOAc), 3.32 (d, 2 H, $J = 5\text{ Hz}$, CH_2Br), and 1.32 ppm (d, 3 H, $J = 6\text{ Hz}$, CH_3CH); 1-bromo-2-propyl acetate nmr (CCl_4) δ 4.05 (m, 3 H, CHBr , and CH_2OAc), and 1.65 ppm (d, 3 H, $J = 6.5\text{ Hz}$, CH_3).

Anal. Calcd for $\text{C}_5\text{H}_9\text{BrO}_2$: C, 33.17; H, 5.01; Br, 44.13. Found: C, 33.11; H, 4.98; Br, 44.16.

Reaction of Acetyl Perchlorate with Epichlorohydrin. Epichlorohydrin (0.0925 g, 1 mmol) was added to a solution of 1 mmol of acetyl perchlorate in carbon tetrachloride with stirring at 0° . After 30 min the reaction mixture was washed with water and dried. The nmr spectrum showed 1-perchlorato-3-chloro-2-propyl acetate and 2-perchlorato-3-chloro-1-propyl acetate in the ratio 1.4:1. The total yield was 93% using chlorobenzene as a quantitative nmr standard: 1-perchlorato-3-chloro-2-propyl acetate nmr (CCl_4) δ 5.10

(m, 1 H, CHOAc), 4.68 (d, 2 H, $J = 5 \text{ Hz}$, CH_2OCIO_3), 3.65 (d, 2 H, $J = 6 \text{ Hz}$, CH_2Cl) and 2.13 ppm (s, 3 H, CH_3COO); 1-perchlorato-2-chloro-1-propyl acetate; nmr (CCl_4) δ 5.20 (m, 1 H, CHOCIO_3) 4.37 (m, 2 H, CH_2OAc), 3.78 (d, 2 H, $J = 6 \text{ Hz}$, CH_2Cl), and 2.08 ppm (s, 3 H, CH_3COO). The infrared spectrum of the mixture of products showed strong bands at 1755 (C=O), and 1280, 1240, 1050 cm^{-1} (OCIO_3).

The solution was added dropwise to 5 ml of a 10% solution of lithium bromide in acetone with stirring at room temperature. The reaction mixture was washed with water and dried. Evaporation of solvent gave 0.186 g (87%) of a mixture of 1-bromo-3-chloro-2-propyl acetate and 2-bromo-3-chloro-1-propyl acetate.

Reaction of Acetyl Perchlorate with 2-Butene Oxide. 2-Butene oxide (0.072 g, 1 mmol) was added to a solution of 1 mmol of acetyl perchlorate with stirring at 0° . After 30 min the solution was washed with water and dried to give a carbon tetrachloride solution of 3-perchlorato-2-butyl acetate in 73% yield: nmr (CCl_4) δ 4.92 (m, 2 H, CHOAc , CHOCIO_3), 2.03 (s, 3 H, CH_3COO), 1.48 (d, 3 H, $J = 6.5 \text{ Hz}$, $\text{CH}_3\text{-CHOCIO}_3$), and 1.28 ppm (d, 3 H, $J = 7 \text{ Hz}$, CH_3CHOAc); ir (CCl_4) 1745 (C=O); 1280, 1240, 1040 cm^{-1} (OCIO_3).

Reaction of Acetyl Perchlorate with Dimethoxymethane. Dimethoxymethane (0.076 g, 1 mmol) was added to a solution of 1 mmol of acetyl perchlorate in carbon tetrachloride with stirring at 0° . After 15 min, nmr showed the disappearance of the starting materials and the formation of methyl acetate (95%) and methoxymethyl perchlorate (83%). The yields were determined by nmr using chloroform as a quantitative standard. Washing with water and filtration of the solution through silica gel to remove formaldehyde polymer gave a solution

of methyl acetate (78%) identified by comparison of spectral and gas chromatographic parameters with those of an authentic sample.

Reaction of Chloromethyl Methyl Ether with Silver Perchlorate. Chloromethyl methyl ether (0.0805 g, 1 mmol) was added to a stirred suspension of 0.30 g (1.5 mmol) of silver perchlorate in 4 ml of carbon tetrachloride. After 30 min, nmr spectra indicated that starting material was consumed, and methoxymethyl perchlorate, identical with the material above, was formed in 81% yield. Solutions fumed in moist air: nmr (CCl_4) δ 5.57 (s, 2 H, CH_2) and 3.67 ppm (s, 3 H, CH_3); ir (CCl_4) 1280, 1260, 1050 cm^{-1} (OClO_3).

Benzoyl Perchlorate. Benzoyl chloride (0.703 g, 5 mmol) in 5 ml of carbon tetrachloride, was added dropwise at 0° with stirring to 1.45 g (7 mmol) of silver perchlorate suspended in 10 ml of carbon tetrachloride. Stirring was continued for 2 hrs. Filtration under anhydrous conditions gave a colorless solution of benzoyl perchlorate which fumed in moist air. The yield was 98% using cyclohexane as quantitative internal nmr standard: nmr (CCl_4) δ 7.4-8.1 (m, Ar), ir (CCl_4), 3080 (w), 1780 (vs), 1590 (m), 1450 (m), 1280 (vs), 1225 (s), 1180 (m), 1050 (s), 950 cm^{-1} (vs).

Reaction of Benzoyl Perchlorate with Methanol. Excess methanol (0.96 g, 30 mmol) was added to 5 mmol of benzoyl perchlorate in carbon tetrachloride prepared as above. The reaction mixture was stirred for 10 min, washed with water and dried. The only product was methyl benzoate (95%).

Reaction of Benzoyl Perchlorate with Isopropyl Ether. Isopropyl ether (0.50 g, 5 mmol) was added to 5 mmol of benzoyl perchlorate in carbon tetrachloride at room temperature. After three hours the reaction, monitored by nmr, was complete and gave isopropyl perchlorate and isopropyl benzoate each in 98% yield (ethylene chloride as quantitative internal nmr standard). The

structure of the products was confirmed by comparison of nmr and ir spectra with those of authentic isopropyl perchlorate and isopropyl benzoate.

Reaction of Benzoyl Perchlorate with Tetrahydrofuran. A solution of 0.36 g (5 mmol) of tetrahydrofuran in 2 ml of carbon tetrachloride was added dropwise with stirring to 5 mmol of benzoyl perchlorate in carbon tetrachloride at 0°. After 30 min the reaction mixture was washed with water, and dried. Nmr spectra of the carbon tetrachloride solution showed 4-perchloratobutyl benzoate (83%) contaminated by a small quantity of polymeric materials showing a broad band in the ether region (3.50 ppm). Filtration through a short column of silica gel removed the latter: nmr (CCl_4) δ 7.2-8 (m, 5 H, Ar); 4.57 (m, 2 H, CH_2OCIO_3), 4.32 (m, 2 H, $\text{CH}_2\text{OCOC}_6\text{H}_5$), and 1.95 ppm (broad m, 4 H, CH_2CH_2); ir (CCl_4) 1735 (C=O), 1295, 1260 cm^{-1} (OCIO_3).

The carbon tetrachloride solution was added dropwise at room temperature to 20 ml of a 10% solution of lithium bromide in acetone. The reaction mixture was stirred for 30 min, washed with water and dried. Evaporation of solvent gave 0.905 g (71%) of 4-bromobutyl benzoate: nmr (CCl_4) δ 7.1-7.8 (m, 5 H, Ar); 4.20 (m, 2 H, $\text{CH}_2\text{OCOC}_6\text{H}_5$); 3.33 (m, 2 H, CH_2Br), and 1.93 ppm (m, 4 H, CH_2CH_2); ir (CCl_4) 1720 cm^{-1} (C=O).

Anal. Calcd for $\text{C}_{11}\text{H}_{13}\text{BrO}_2$: C, 51.40 H, 5.10 Br, 31.10. Found: C, 51.42 H, 4.93; Br, 31.20.

N,N-Diethylcarbamoyl Perchlorate. Diethylcarbamoyl chloride (0.675 g, 5 mmol) dissolved in 5 ml of carbon tetrachloride was added dropwise with stirring, over a 10 min period, to 1.20 g (6 mmol) of silver perchlorate suspended in 15 ml of carbon tetrachloride at 0°. The reaction mixture was stirred for 30 min and 10 ml of carbon tetrachloride was added to give a solution of N,N-diethylcarbamoyl perchlorate in 82% yield (ethylene chloride

as quantitative nmr standard:: nmr (CCl_4) δ 3.33 (q, 4 H, $J = 7$ Hz, N-CH_2) and 1.25 ppm (t, 6 H, $J = 7$ Hz, CH_3); ir (CCl_4) 2960 (m), 1782 (vs), 1480 (m), 1460 (m), 1420 (m), 1390 (m), 1370 (w), 1320 (w), 1280 (vs), 1220 (m), 1140 (s), 1100 (s), 1050 (s), 1020 (m), 960 (w), 900 cm^{-1} (s).

Reaction of N,N-Diethylcarbamoyl Perchlorate with Methanol. Excess methanol (0.96 g, 0.03 mol) was added to a solution of N,N-diethylcarbamoyl perchlorate in carbon tetrachloride, prepared as above, with stirring at 0° . The reaction mixture was stirred for 30 min, washed with water and dried. Evaporation of solvent gave 0.517 g (96%) of N,N-diethyl methyl carbamate identified by spectral comparison with an authentic sample described below.

N,N-Diethyl Methyl Carbamate. Methyl chloroformate (9.45 g, 0.1 mol) was added dropwise with stirring at $0-5^\circ$ to a solution of 7.3 g (0.1 mol) of diethyl amine and 3.9 g (0.1 mol) of sodium hydroxide in 25 ml of water. The reaction mixture was stirred for 30 min and extracted with methylene chloride and distilled to give 10.3 g (79%) of N,N-diethyl methyl carbamate, bp $66-68^\circ$ (26 mm); nmr (CCl_4) δ 3.57, (s, 3 H, OCH_3), 3.17 (q, 4 H, $J = 7$ Hz, N-CH_2); and 1.10 ppm (t, 6 H, $J = 7$ Hz, CH_3); ir (CCl_4) 1700, 1280, 1180 cm^{-1} (CON).

Reaction of N,N-Diethylcarbamoyl Perchlorate with Tetrahydrofuran.

A solution of 0.36 g (5 mmol) of tetrahydrofuran in 3 ml of carbon tetrachloride was added dropwise with stirring at 0° to a solution of N,N-diethylcarbamoyl perchlorate prepared as above. After 30 min the solution was washed with water and dried to give a solution of 4-perchloratobutyl N,N-diethylcarbamate (75% yield by nmr, chlorobenzene quantitative standard): nmr (CCl_4) δ 4.52 (t, 2 H, $J = 6$ Hz, CH_2OClO_3), 4.00 (t, $J = 6$ Hz, 2 H, CH_2OCON), 3.18 (q, 4 H, $J = 6.5$ Hz, CH_2N), 1.83 (m, 4 H, CH_2CH_2) and 1.12 ppm

(t, 6 H, $J = 6.5$ Hz, CH_3); ir (CCl_4) 1695 (OCON), 1280 and 1040 cm^{-1} (OClO_2).

The carbon tetrachloride solution of the product was added to 20 ml of a 10% solution of lithium bromide in acetone. After 30 min, the reaction mixture was washed with water and dried. Evaporation of solvent gave 0.176 g (70%) of N,N-diethyl 4-bromobutyl carbamate as a pale yellow oil. An analytical sample was collected by glpc using a 6 ft x 1/4" aluminum column packed with 10% QF-1 on 60/80 mesh chromosorb W at 150°: nmr (CCl_4) δ 3.97 (t, 2 H, $J = 6$ Hz, CH_2OCON); 3.33 (t, 2 H, $J = 6$ Hz, CH_2Br) 3.17 (q, 4 H, $J = 7$ Hz, N- CH_2); 1.83 (m, 4 H, CH_2CH_2) and 1.10 ppm (t, 6 H, $J = 7$ Hz, NCH_2CH_3); ir (CCl_4) 1695, 1180 cm^{-1} (OCON).

Anal. Calcd for $\text{C}_9\text{H}_{18}\text{BrNO}_2$: C, 42.86; H, 7.2; Br, 31.69; N, 5.6.

Found: C, 42.56; H, 6.87; Br, 31.58; N, 5.74.

Reaction of Ethyl Ether with Dichlorine Heptoxide. Ethyl ether (0.0888 g, 1.2 mmol) was added to 4 ml of 0.3 M dichlorine heptoxide in carbon tetrachloride² at room temperature. Aliquots were removed periodically, washed with water, dried, and analyzed by nmr for ethyl perchlorate² (% yield) and ethyl ether (% recovery) respectively as follows: 10 min, 33, 57; 2 hrs, 53, 37; 18 hrs, 59, 26; 66 hrs, 67, 18. Ethyl acetate was also formed, with a yield of 2-3% in 66 hrs. A small acid signal also appeared (before water treatment of the aliquots) at δ 15.5-16.0 as the reaction progressed, and its formation was accompanied by a downfield shift of 0.28 ppm for the methylene hydrogens of ethyl ether.

Reaction of Propyl Ether with Dichlorine Heptoxide. Propyl ether (0.1224 g, 1.2 mmol) was added to 4 ml of 0.3 M dichlorine heptoxide in carbon tetrachloride and the reaction was followed by nmr, as in the preceding example. In 15 hrs, the spectrum showed propyl perchlorate² (49% yield), isopropyl

perchlorate² (13%) and propyl ether (33%); in 66 hrs, no significant further changes took place. An acid signal (δ 15.9) and downfield shift of the α -hydrogen signal of propyl ether were observed before water treatment of the samples. In a control experiment, no reaction was observed between propyl perchlorate and propyl ether under the same conditions.

Reaction of Tetrahydrofuran with Dichlorine Heptoxide. Tetrahydrofuran (0.176 g, 2.4 mmol) in 1 ml of carbon tetrachloride was added dropwise with stirring at 0° to 8 ml of 0.3 M dichlorine heptoxide in carbon tetrachloride. After 15 min, the solution was washed with water and dried over magnesium sulfate to give a solution of 1,4-butane diperchlorate² (83% yield using chlorobenzene as quantitative nmr standard). No other products were detected by nmr or ir.

Reaction of Trimethylene Oxide with Dichlorine Heptoxide. A solution of 0.087 g (1.5 mmol) of trimethylene oxide in 2 ml of carbon tetrachloride was added dropwise with stirring to 5 ml of 0.3 M dichlorine heptoxide in carbon tetrachloride at 0°. After 30 min, the solution was washed with water, dried over sodium sulfate and filtered through silica gel to remove small quantities of polymeric material. The nmr spectrum of the resulting solution showed only 1,3-propanedipерchlorate (55% yield using chlorobenzene as quantitative standard): nmr (CCl_4) δ 4.55 (t, 4 H, $J = 6$ Hz, CH_2OClO_3), and 2.28 ppm (quintet, 2 H, $J = 6$ Hz, $\text{C}-\text{CH}_2-\text{C}$; ir (CCl_4) 1290, 1270, 1230, 1010, 1030 cm^{-1} (OClO_3).

Reaction of Isopropyl Pentyl Ether with Dichlorine Heptoxide. Isopropyl pentyl (0.078 g, 0.6 mmol) was stirred with 2 ml of 0.3 M dichlorine heptoxide solution in carbon tetrachloride for 18 hrs at room temperature. A small quantity of a colorless oil separated, soluble in CDCl_3 , which was identified as 2,2-dipерchloratopropane by nmr⁹. The carbon tetrachloride layer was

washed with water and dried. Nmr showed a 22% yield of isopropyl perchlorate, 11% pentyl perchlorate and 18% isopropyl pentyl ether.

Reaction of Dimethoxymethane with Dichlorine Heptoxide. Dimethoxymethane (0.091 g, 1.2 mmol) was added to 4 ml of 0.3 M dichlorine heptoxide in carbon tetrachloride. The reaction, followed by nmr, was complete in 5 days to give methyl perchlorate (86%) and methoxymethyl perchlorate (78%).

Reaction of Isopropyl Ether with Dichlorine Heptoxide. Isopropyl ether (0.061 g, 0.6 mmol) was added to 2 ml of 0.3 M dichlorine heptoxide in carbon tetrachloride with stirring at 0°. In 5 min, the solution became pale yellow-green and after 10-15 min a colorless oil separated and the solution became colorless. The solution contained isopropyl perchlorate (10% yield by nmr) and isopropyl ether (25%). The oil was identified as 2,2-diperchloratopropane⁹: nmr (CDCl₃) δ 2.60 ppm (s). In another experiment, water and 2,4-dinitrophenylhydrazine reagent were added to the crude product mixture to give 0.086 g (60%) acetone 2,4-dinitrophenylhydrazone.

Reaction of Epoxides with Dichlorine Heptoxide. 2-Butene oxide (0.0353 g, 0.49 mmol) was added with stirring to 2 ml of 0.3 M dichlorine heptoxide in carbon tetrachloride at 0°. The solution was stirred 24 hrs at ambient temperature. The solution was separated from a dark insoluble oil, washed with water, and dried over sodium sulfate. Spectra were consistent with the 2,3-butanediperchlorate structure (30% yield by nmr): nmr (CCl₄) δ 1.58 (d, 6 H, J = 6 Hz, CH₃) and 5 ppm (m, 2 H, CH); ir (CCl₄) 1280, 1240, 1040 cm⁻¹ (ClO₄).

Equimolar amounts of 2-butene oxide and dichlorine heptoxide by this procedure gave a mixture with two additional methyl doublets.

Ethylene oxide, propylene oxide and epichlorohydrin reacted on mixing with dichlorine heptoxide, but nmr spectra indicated complex mixtures. The

ir spectra showed strong perchlorate bands at approximately 1280, 1240 and 1020 cm^{-1} .

References

1. This work was supported by the Office of Naval Research.
2. K. Baum and C. D. Beard, J. Amer. Chem. Soc., submitted.
3. C. D. Beard and K. Baum, J. Amer. Chem. Soc., submitted.
4. M. Schmeisser, Angew. Chem., 67, 493 (1955).
5. H. Burton and P. F. G. Praill, J. Chem. Soc., 2034 (1950); Ibid, 529, (1951); Ibid, 827 (1953).
6. C. Cauquil, R. Barrera and H. Barrera, Bull. Soc. Chim. Fr., 1111 (1953).
7. G. A. Olah and H. W. Quinn in "Friedel-Crafts and Related Reactions", G. A. Olah, Ed., Vol. IV, p. 260, Interscience Publishers, New York, (1965).
8. G. A. Olah, S. J. Kuhn, W. S. Tolgyesi and E. B. Baker, J. Amer. Chem. Soc., 84, 2733 (1962).
9. K. Baum, J. Amer. Chem. Soc., 92, 2927 (1970).
10. R. L. Burwell, Jr., Chem. Rev., 54, 615 (1954).
11. F. Johnson in "Friedel-Crafts and Related Reactions", G. A. Olah, Ed., Vol. IV, p. 1, Interscience Publishers, New York (1965).
12. M. H. Karger and Y. Mazur, J. Org. Chem., 36, 532 (1971).
13. N. C. Deno and N. H. Potter, J. Amer. Chem. Soc., 89, 3550 (1967).
14. F. Westheimer, Chem. Rev., 45, 419 (1949).